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Environmental Risk Assessment Report:

Octamethylcyclotetrasiloxane

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Our work includes tackling flooding and pollution incidents, reducing industry's impacts on the environment, cleaning up rivers, coastal waters and contaminated land, and improving wildlife habitats.

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Steve Killeen

Head of Science

Executive summary

The Environment Agency's environmental risk assessment for octamethylcyclotetrasiloxane (D4) is based on the methods outlined in the European Union (EU) Technical Guidance Document (TGD) for the risk assessment of new and existing chemicals. The persistence, bioaccumulative, and toxic (PBT) status is assessed, and a 'quantitative' risk assessment made by comparison of exposure with effects.

Persistent, bioaccumulative, and toxic status assessment

The persistence of D4 in sediment means it potentially meets the criteria for a PBT substance. It is unlikely to meet the persistent organic pollutants (POPs) screening criteria in long-range transport.

Laboratory studies indicate that D4 is not readily biodegradable in aquatic systems. However, it is difficult to interpret some of the results because of the rapid loss of D4 through volatilisation, but the final products of the hydrolysis of D4 are not thought to have PBT properties. Based on the rapid hydrolysis, D4 is not persistent or very persistent in surface water. However, the persistence in sediment is not as clear. Although D4 is highly volatile and degrades relatively rapidly in surface water by hydrolysis, it has a high log octanol–water partition coefficient (Kow) value and so it is also expected to adsorb onto sediment. Very limited data are currently available as to the persistence of D4 adsorbed onto sediment, but they suggest that the half-life may approach 120 days at room temperature. Thus, D4 could potentially meet the criteria for persistence in sediment. Although volatilisation from water is likely to be the dominant removal mechanism of D4 from aquatic systems, it is detected in some sediments. However, the high rate of volatilisation is likely to limit the amount of D4 that ultimately reaches the sediment compartment.

The bioconcentration factor (BCF) for D4 in fish is 12,400 l/kg, and so it meets the very bioaccumulative criterion.

D4 has a long-term fish no-observed-effect concentration (NOEC) □4.4 µg/l, a fish NOEC of 4.4 µg/l from a 14-day prolonged acute toxicity study, and a long-term NOEC of 7.9 µg/l from a Daphnia magna reproduction study. In addition, it is classified as a category 3 reprotoxicant. Therefore D4 meets the toxic criterion.

The overall conclusions of the PBT assessment are that D4 potentially meets the criteria for a PBT substance when the persistence in sediment is considered, but this is based on a poorly reported preliminary study. However, even though the amount of D4 that reaches the sediment compartment is likely to be limited, further experimental and modelling work to evaluate its persistence in sediment is in progress. Thus the PBT assessment should be revisited once the results are available.

Quantitative risk assessment

The risks from the normal use of D4 to water, sediments, soil, and predators are assessed using standard models and the information available. The property data set is reasonably complete, but in some areas further information will be valuable. This assessment therefore makes recommendations about the significance of the gaps and uncertainties in the data, and suggests the focus of further research.

The main use of D4 is as an intermediate in the production of other chemicals (silicone polymers and synthetic amorphous silica), in personal care products (e.g. cosmetic products and skin- and hair-care products), and in household products (e.g. cleaning

products). Use as an intermediate to make silicone polymers effectively consumes the D4, although trace amounts in the final products can be subsequently released to the environment. Use of D4 in personal care and household products results in widespread exposure to it in the environment.

Estimates of the potential emissions to the environment from D4's key life-cycle stages are based on industry research and Emission Scenario Documents or, in the absence of any other information, worst-case default assumptions. Where relevant, monitoring data available for some life-cycle stages are also taken into account. Risk characterisation ratios for some D4 life-cycle stages relevant to the United Kingdom (UK) are above one, which indicates an unacceptable risk to the environment. In the UK, the most significant part of the life cycle is production and on-site use as an intermediate, and this has the highest priority for further work. In addition, uncertainties in the assessment for predators in general should be addressed. The risk to humans exposed to D4 via the environment are assessed and the results show no concerns for local or regional exposure.

Some information provided by industry is treated as confidential and not given in this report, although the data are used to develop appropriate emission scenarios. These data are included in a confidential annex that supports the assessment, which is available via the Project Manager, where appropriate.

The overall conclusions of the risk assessment are:

- No risks from off-site use as an intermediate (both wet and dry processes), from formulation and use in both personal care products and household products, and from regional sources of D4 are identified for air, water, sediment, and the terrestrial compartments. There are also no risks for humans exposed to D4 via the environment.
- Possible risks are identified from the production and on-site use as an intermediate at the UK production site, and apply to freshwater, freshwater sediment, predators, marine waters, marine sediments, marine predators, and top predators. These conclusions are based on the best information available, but this is limited and hence there is significant uncertainty in the conclusions. The receiving fresh water, which is subject to local Environment Agency regulation, is a relatively non-standard environment, and dilution into the sea is possibly higher than the default value used.
- Further information required to reduce these uncertainties should include clarification of the emissions from the production site in the UK. This could be statistically analysed site-specific data on emissions, in compliance with the TGD (e.g. further effluent monitoring or monitoring of the receiving water).
- Uncertainties are associated with the assessment for predators because of both the BMFs and the predicted no-effect concentrations (PNECs) used.
- Subject to further information on these uncertainties, more testing may be required to revise the predicted effect concentrations (PECs), such as long-term toxicity tests with both Lumbriculus variegatus and Hyalella azteca (or similar) using spiked sediment.
- However, for the production and on-site use as an intermediate scenario, revision of the PNEC for sediment alone is unlikely to result in a risk characterisation ratio <1 unless further data are obtained to refine the PEC for sediment.

- Industry is undertaking a voluntary test programme to address some of these issues. It is understood that further studies for D4 currently being considered, or underway, are:
- evaluation of additional degradation pathways;
- degradation in sediment under aerobic and anaerobic conditions;
- further modelling of the environmental distribution and overall fate;
- sediment toxicity study with Lumbriculus spp.;
- in vivo metabolism and kinetics study with fish following oral exposure;
- bioaccumulation using physiologically based pharmacokinetic (PBPK) models of fish;
- bioaccumulation using extensions of the PBPK model for fish and mammals to other species;
- environmental monitoring (including air, sewage effluent, river water, sediment, and biota), such as a mussel-screening study, a river distribution and die-away study downstream from a known point source with site-specific monitoring, and a long-term monitoring programme that is likely to involve:
  - time trends using freshwater and marine sediment cores from local, regional, and remote locations and from archived biota samples,
  - spatial distributions using sediment and biota samples along transects of freshwaters from local, regional, and remote locations,
  - marine samples (sediment and biota) from regional and remote locations,
  - air samples from local, regional, and remote locations.
- development of analytical methodologies to support these studies.

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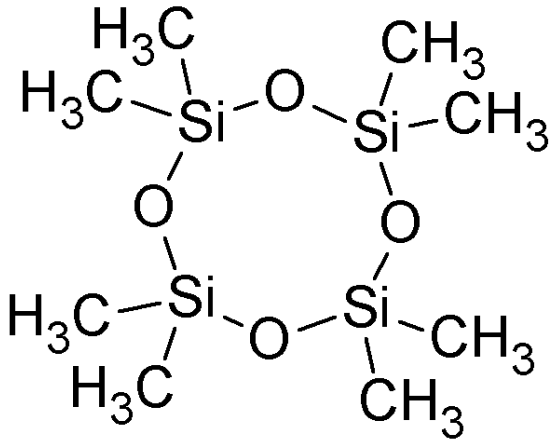
Douglas Gray at the Health & Safety Executive produced the review of mammalian toxicity data and the human health risk characterisation.

Contents

1 General octamethylcyclotetrasiloxane information

1.1 Identification of octamethylcyclotetrasiloxane

- CAS No: 556-67-2
- EINECS No: 209-136-7
- EINECS Name: octamethylcyclotetrasiloxane
- Molecular formula: C8H24O4Si4
- Molecular weight: 296.62 g/mole
- Smiles notation: C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1
- Structural formula:



Other names, abbreviations, trade names, and registered trademarks for octamethylcyclotetrasiloxane (D4) in current use include (CES, 2005b):

- cyclic dimethylsiloxane tetramer
- Cyclen D4/OMCTS
- Cyclen D4/OMCTS WN
- cyclomethicone1

[1]Cyclomethicone is the 'old International Nomenclature Cosmetic Ingredient (INCI) name, which is no longer used for D4. It is a generic name used for mixtures of cyclic siloxanes and typically represents a mixture of D4, decamethylcyclopentasiloxane, and dodecamethylcyclohexasiloxane.

- cyclotetrasiloxane, octamethyl-
- cyclotetrasiloxane2
- D4
- Dow Corning 244
- KF 994
- DC 344
- DC 244
- Dow Corning 344
- NUC silicone VS 7207
- Oel Z020
- OMCTS
- SF 1173
- Tetramere D4/OMCTS
- Tetramere D4/OMCTS Silbione
- TSF 404
- Volasil 244
- VS 7207.

Names, abbreviations, trade names, and registered trademarks no longer in current use (or their current use cannot be confirmed) are given below. Although these names are no longer used, it is useful to include them here as they may be referred to in some of the older literature:

- Abil K4
- Dabco DC 5258
- DC 5258
- LS 8620
- Mirasil CM 4NSC 345674
- SH 244
- SH 344
- Silbione V 2
- Silbione 70045V2
- Tetracyclomethicone
- Y 7175

[2] Cyclotetrasiloxane is the INCI name used to identify D4 in cosmetic products.

- UC 7207
- Union carbide 7207.

In Europe, octamethylcyclotetrasiloxane is commonly referred to as D4 and this abbreviation is used in this assessment.

Also relevant to this assessment is the CAS Number 69430-24-6. This relates to a mixture of dimethyl-substituted cyclosiloxanes with less than eight (typically between three and seven) dimethylsiloxane groups present in the ring (Environment Canada, 2008). The name commonly associated with this CAS Number is cyclomethicone, but other names include cyclopolydimethylsiloxane, cyclopolydimethylsiloxane (DX), cyclosiloxanes di-Me, dimethylcyclopolysiloxane, polydimethylsiloxy cyclics, polydimethylcyclosiloxane, and mixed cyclosiloxane. The D4 in cyclomethicone is accounted for in this assessment.

1.2 Purity, impurity, and additives

1.2.1 Purity and impurities

The purity of D4 is >96 to >99. The major impurity is decamethylcyclopentasiloxane (D5).

1.2.2 Additives

No additives are present in the commercial substance.

1.3 Physicochemical properties

1.3.1 Physical state (at normal temperature and pressure)

D4 is a liquid at normal temperature and pressure (IUCLID, 2000).

1.3.2 Melting point

The accepted value for the melting point of D4 is 17.7°C (IUCLID, 2005). IUCLID (2000, 2005) and Merck (1996) also give a value of 17.5°C.

A melting point of 17.7°C is used in this assessment.

1.3.3 Boiling point

The boiling point of D4 is reported as 175°C at atmospheric pressure (OECD, 1995; Merck, 1996; IUCLID, 2000, 2005). Chandra (1997) reviews the available measured data and

estimation methods for D4 and reports that the measured boiling point is 176°C and the best estimate for the boiling point is 183°C.

Merck (1996) also gives a value for the reduced pressure boiling point of 74°C at 20 mmHg.

A boiling point of 175°C at atmospheric pressure is assumed in this assessment.

1.3.4 Density

The density of D4 is reported as 0.96 g/cm^3 at 20°C (IUCLID, 2000) and 0.949 g/cm^3 at 25°C (IUCLID, 2005). Merck (1996) gives the relative density as 0.9558. Chandra (1997) reviews the measured data and estimation methods available for D4 and reports that the measured density at 20°C is 0.953 g/cm^3 and the best estimate for the density at 20°C is 0.959 g/cm^3.

The value of 0.95 g/cm^3 at 25°C is used in this assessment.

1.3.5 Vapour pressure

Flaningam (1986) measured the vapour pressure of D4 using an ebulliometer. The D4 tested was distilled prior to use and 99.47 per cent pure. The vapour pressure of D4 was determined over a temperature range of 361–469 K (88–196°C). The corresponding pressure range was 5.4–133 kPa at these temperatures. The data were fitted to the Antoine equation:

$$\ln P_v = A - B/(T + C) \quad (1.1)$$

where P_v is the vapour pressure in Pa, T is the temperature in Kelvin, A is a constant (= 20.4534 for D4), B is a constant (= 3128.52 for D4), and C is a constant (= –98.093 for D4).

The standard deviation in the experimental vapour pressure for Equation (1.1) is given as 0.034 kPa.

Using Equation (1.1), the vapour pressure of D4 can be estimated as 82 Pa at 20°C and 122 Pa at 25°C.

Flaningam (1986) also fitted the vapour pressure data (along with other published vapour pressure data for D4) to the AIChE DIPPR[3] equation. The root mean square percentage error in this method is 1.36 over the temperature range 280–586 K.

$$\ln P_v = A + B/T + C \times \ln(T) + D \times T^E \quad (1.2)$$

where P_v is the vapour pressure in Pa, T is the temperature in Kelvin, A is a constant (= 95.191 for D4),

B is a constant (= –9,504.6 for D4), C is a constant (= –10.246 for D4),

D is a constant (= 1.04739×10^{-17} for D4), and

E is a constant (= 6 for D4).

Using Equation (1.2), the vapour pressure of D4 can be estimated as 96 Pa at 20°C and 139 Pa at 25°C. The agreement between the vapour pressures obtained using the DIPPR method and the Antoine method is good. Although the paper indicates that within the range of the experimental data generated the Antoine equation is more accurate, the temperature

[3]American Institute of Chemical Engineers – Design Institute for Physical Properties.

range for which the DIPPR equation is valid covers ambient environmental temperatures and so these latter values are considered more reliable for use in this risk assessment.

Another value for the vapour pressure for D4 of 132 Pa at 25°C is given in IUCLID (2005). This value is an interpolated value derived from a temperature–vapour pressure correlation (the AIChE DIPPR method) using critically evaluated data obtained over the temperature range 17.6–313°C. The actual data used in the correlation and the fitted parameters that result are not reported. However, as the temperature range covered appears to be larger than that in the Flaningam (1986) paper, this value is taken as the more reliable one (although there is very good agreement between the two studies).

Chandra (1997) reviews the available measured data and estimation methods for D4 and reports that the measured vapour pressure at 25°C is 0.99 mmHg (~132 Pa) and the best estimate for the vapour pressure at 25°C is 1.67 mmHg (~223 Pa). The measured vapour pressure appears to be based on the data of Flaningam (1986).

Kent *et al*. (1994) give the vapour pressure as 0.68 mmHg (91 Pa) at 20°C based on the results from Flaningam (1986).

The vapour pressure of D4 at 25°C can be estimated as 157 Pa (1.18 mmHg) using the United States Environmental Protection Agency (USEPA EPI) (v3.12)] estimation software. The value represents the mean of estimates using the Antoine method and the modified grain method and is based on an experimental boiling point of 175.8°C.

The database within the EPI software also contains an experimental value for the vapour pressure of D4. This is 140 Pa (1.05 mmHg) extrapolated to 25°C and is referenced to Flaningam (1986).

A further vapour pressure of 100 Pa at 20°C is reported in IUCLID (2005; referenced to OECD but no further details of this value are available).

A vapour pressure of 132 Pa at 25°C, as recommended in IUCLID (2005) and Chandra (1997), is assumed in this assessment. This value is derived from a temperature–vapour pressure correlation using critically evaluated data.

1.3.6 Water solubility

Varaprath *et al*. (1996) determined the water solubility of D4 using a slow-stirring method to avoid the formation of colloidal suspensions. The method involved adding D4 to the surface of the water (1500 ml of water in a 2 l flask; sufficient D4 was added to cover the water) and gently stirring the water phase (avoiding cavitation and turbulence). The test was carried out at 23°C. At various time points, samples were run off from the bottom of the flask via a tap and analysed for D4. A preliminary investigation into the feasibility of the method found the average concentration of D4 in the water phase was constant from day 21 to day 27, with a mean (± standard deviation) concentration of 53.1 ± 6.6 µg/l and 56.0 ± 3.5 µg/l using two different methods of analysis. The water solubility is given as 56.2 ± 2.5 µg/l at 23°C based on three determinations.

Two other methods were used by Varaprath *et al.* (1996) to determine the water solubility of D4. The first involved the partitioning between D4-laden air and water and the second involved partitioning between D4 in a solvent and water. Aggregates of D4 were thought to form in the water using both of these methods, but the true solubility is estimated as around 50 µg/l using these methods.

Hobson (1995), Hobson and Siberhorn (1995), and Chandra (1997) report the results of unpublished studies to determine the solubility of D4 in freshwater and seawater. These give the water solubility as 74 µg/l in freshwater and 33 µg/l in seawater, in good agreement with the values determined by Varaprath *et al*. (1996).

Other reported values for the water solubility (from unpublished studies) are given as 0.07 mg/l at 25°C and ca. 0.02 mg/l at 25°C (IUCLID, 2005).

Earlier studies report the water solubility of D4 to be significantly higher than those given in the Varaprath *et al.* (1996) study. For example, Vogel and Stark (1964) reported the solubility of D4 to be around 2 mg/l at 25°C. However, it is likely that suspensions of D4 were present in these earlier studies and so the values probably overestimate the true solubility of D4.

With the USEPA EPI (v3.12) estimation software a water solubility of 0.054 mg/l at 25°C is estimated for D4 using a log octanol–water partition coefficient (K_{ow}) of 5.10 (the method applies a correction for cyclic siloxanes).

A second estimate for the water solubility of D4 of 0.17 mg/l at 25°C is also obtained from the USEPA EPI program. This value is estimated by a fragment approach.

The database within the EPI software also contains an experimental value for the water solubility of D4 of 0.005 mg/l at 25°C. However given the other data available, this value probably refers to dodecamethylcyclohexasiloxane [D6 (see Environment Agency, 2008b)] rather than D4.

Chandra (1997) reviewed the available measured data and estimation methods for D4 and reported that the measured water solubility at room temperature was 0.056 mg/l and the best estimate for the water solubility at 25°C was 0.055 mg/l.

A water solubility of 0.056 mg/l at 23°C will be assumed in this assessment. This is based on the Varaprath *et al*. (1996) study and the review by Chandra (1997).

1.3.7 *n*-Octanol–water partition coefficient

Two experimental values for the log K_{ow} of D4 are available. The first study (Bruggeman *et al.*, 1984) determined the log K_{ow} to be 4.45 using a high performance liquid chromatography (HPLC) retention time method. A homologous series of *n*-alkylbenzenes were used as reference compounds. The second (unpublished) study gave the log K_{ow} value of D4 as 5.1 (IUCLID, 2005). Few other details of this study are currently available.

As D4 undergoes hydrolysis (see Section 0), it is not clear from the information reported if the possibility of this was accounted for in these studies.

USEPA EPI (v3.12) estimation software gives a log K_{ow} of 5.09 for D4. This program estimates the log K_{ow} from the chemical structure using a fragment method.

Further work to investigate the log K_{ow} for D4 is being undertaken on a voluntary basis by the industry. Preliminary results from some of this work were available in a poster presentation (Xu and Kozerski, 2007). The log K_{ow} values reported for D4 are 6.49 using a slow-stirring method and 7.00 using a syringe method. For comparison, Xu and Kozerski (2007) also calculated a value for the log K_{ow} using linear solvation energy relationships. The value for D4 this method was 6.31. It is understood that the analytical methodology used in the slow-stirring method was based on parent-compound analysis to avoid complications from hydrolysis of D4 or of more soluble impurities. No further details of these studies are currently available.

Xu *et al*. (2007) report the same log K_{ow} for D4 of 6.49 from the slow-stirring method based on a study by Kozerski and Shawl (2007). Again, no further details of this study are currently available.

Insufficient information is available to validate fully the available log K_{ow} values. Recent work by Xu and Kozerski (2007) indicates that the log K_{ow} value may be substantially higher than found in some of the earlier studies. A log K_{ow} value of 6.49 (obtained using a slow-stirring method designed to avoid problems associated with hydrolysis of D4) is used in the assessment. This value is also self-consistent with some of the other partition coefficients used for D4.[4] However, to recognise the uncertainty in the log K_{ow} value, an analysis was carried out to assess the sensitivity of the assessment of to a lower log K_{ow} value of 5.1 (see Appendix A).

As experimental values are available for some of the key partition coefficients that can be derived from log K_{ow} in the risk assessment

process, notably fish bioconcentration factor (BCF) and organic carbon–water partition coefficient (K_{oc}), the actual value chosen for log K_{ow} does not affect these parameters.

1.3.8 Hazardous physicochemical properties

1.3.8.1 Flash point

IUCLID (2005) gives the flash point for D4 as 61°C (open cup) and 51°C, 55°C, and 57°C (all closed cup values).

1.3.8.2 Autoignition

The auto ignition temperature is 384–387°C (IUCLID, 2005).

1.3.8.3 Explosivity

No information is available.

1.3.8.4 Oxidising properties

No information is available. D4 is not expected to have oxidising properties.

[4]For example, a log K_{ow} of 7 is estimated using the log K_{oa} of 4.34 at 25°C (see Section 0) and the log K_{aw} of 2.69 at 25°C (see Section 0). This shows that the measured log K_{ow} of 6.49 is reasonably consistent with the other partition coefficients considered.

1.3.9 Other relevant physicochemical properties

1.3.9.1 Granulometry

D4 is a liquid at normal temperature and pressure.

1.3.9.2 Surface tension

The surface tension of D4 is 18.5 mN/m at 20°C and 18.3 mN/m at 25°C (Dow Corning internal data; CES, 2005b).

1.3.9.3 Henry's law constant

Kochetkov *et al*. (2001) determined the Henry's law constant of D4 using two different methods. The first was a static method in which a saturated solution of D4 in water was equilibrated with air in the headspace of a sealed container for 48 hours and then the equilibrium concentration of D4 in each phase determined. To avoid the formation of colloidal suspensions of D4 in the water phase, the saturated solution was initially prepared by gentle shaking for two days, followed by a four day settling period; it was finally filtered (0.45 µm) to remove any microemulsions prior to use. The second method was a vapour entry loop method specifically designed to avoid having to add the D4 directly to water (and hence avoid any colloidal emulsion formation). In this method the vapour phase was essentially saturated with D4 by bubbling air though pure D4 and then a portion of this saturated vapour was continuously circulated through water in a sealed system for 48 hours. At the end of this period the concentrations of D4 in both the water and air phases were determined. All experiments were carried out at 28°C.

The values (mean ± standard deviation) for the dimensionless Henry's Law constant (or air–water partition coefficient, K_{aw}) determined for D4 are 23 ± 7 (equivalent to a Henry's law constant of 57,560 Pa m^3/mol) in the static method and 24 ± 3 (equivalent to a Henry's law constant of 60,060 Pa m^3/mol) in the vapour entry loop method. Very good agreement was therefore obtained using the two methods. A reference substance (benzene) was also tested using the same methods. These gave dimensionless Henry's law constants of 0.25 and 0.19, respectively, which agree well with literature values (0.19–0.23).

Hamelink *et al.* (1996) also measured the Henry's law constant of D4. Initial experiments were carried out using a static system over 48 hours. In this system D4 (as a solution in methanol) was added to the water phase in a glass syringe that contained 25 ml of water and 25 ml of air. The system was allowed to equilibrate for 48 hours at 20°C and then the concentration of D4 in both the air and water phase determined. The initial concentration of D4 in the water phase was 40 µg/l. The actual concentration of methanol in the system is not given but, based on the stock solution (100 ppm of D4 in methanol) used in this study it was around 0.4 ml/l. The mean (± standard deviation) dimensionless Henry's law constant obtained using this method was 9.1 ± 1.2 at 20°C (equivalent to a Henry's law constant of 22,177 Pa m^3/mol).

A second series of experiments was carried out using the same test system to investigate if equilibrium was reached within the 48 hour period. In this experiment samples of the water and air phases were analysed at 24 hour intervals for up to 96 hours. Again, methanol was present in the test system [in this case the actual concentration of the stock solution was not clear (several solutions from 5 to 500 ppm of D4 in methanol were prepared)]. The results of

this experiment show that the dimensionless Henry's law constant appear to increase with time, giving mean (± standard deviation) values for the dimensionless Henry's law constant of 5.0 ± 0.8, 9.7 ± 2.1, 13.7 ± 4.1, and 17.0 ± 2.8 after 24, 48, 72, and 96 hours equilibration at 20°C. These values are equivalent to Henry's law constants of 12,180, 23,630, 33,370, and 41,410 Pa m^3/mol, respectively.

To ensure that equilibrium was reached within a relatively short period (i.e. 48 hours) a further series of experiments was carried out using a modified test system in which the glass syringe was slowly rotated (ten revolutions per minute) at an angle of 10° from the vertical to mix the contents gently. In addition, in these studies the volume of water in the system was increased to 80 ml and the volume of air decreased to 20 ml. The initial concentration of D4 in the system was 50 µg/l and methanol was again present in the water phase (the amount is unclear). This system reached equilibrium after 48 hours (giving a mean dimensionless Henry's law constant of 5.62 ± 0.97). Experiments were also carried out using this system to investigate the effect of the initial concentration of D4 on the determined Henry's law constant. No measurable effect occurred over the concentration range 4.0–32 µg/l (the dimensionless Henry's law determined over this concentration range was in the range 1.91 to . The overall mean (± standard deviation) value for the dimensionless Henry's law constant derived using this system at five different concentrations is 3.4 ± 1.37 at 20°C (equivalent to a Henry's law constant of 8280 Pa m^3/mol).

Experiments using a similar test system (initial D4 concentration 40 µg/l) with laboratory water, synthetic sea water, and water supplemented with around 100 mg/l of humic acids resulted in mean (± standard deviation) dimensionless Henry's law constants of 3.0 ± 1.1, 10.5 ± 7.2, and 27.8 ± 2.0–34.2 ± 6.4, respectively, at 20°C (two experiments were carried out with humic acids). These are equivalent to Henry's law constants of 7260, 25,580, and 67,720–83,310 Pa m^3/mol, respectively.

Hamelink *et al*. (1996) also investigated the effect of temperature on the measured Henry's law constant. The initial D4 concentration was 40 µg/l and the mean (± standard deviation) dimensionless Henry's law constants obtained are 1.4 ± 0.1 at 10°C, 2.4 ± 0.8 at 15°C, 3.0 ± 1.1 at 20°C, and 4.8 ± 2.6 at 25°C. These are equivalent to Henry's law constants of 3180, 5700, 7260, and 11,840 Pa m^3/mol, respectively.

The Henry's law constant is estimated as 0.087 atm m^3/mol (8815 Pa m^3/mol) using the using the USEPA EPI (v3.12) estimation software. The value is estimated from the chemical structure using the bond contribution method.

Using a water solubility of 0.056 mg/l at 23°C and a vapour pressure of 132 Pa at 25°C, the Henry's law constant is estimated as 699,200 Pa m^3/mol, considerably higher than the experimental values quoted above.

Further work to investigate the Henry's law constant for D4 is being undertaken on a voluntary basis by the industry. Preliminary results from some of this work were made available in a poster presentation (Xu and Kozerski, 2007). This presentation reports values for the dimensionless Henry's law constant of 500 (reported as a log value of 2.70) using a syringe method, and 126 (reported as a log value of 2.10) calculated using a linear solvation energy relationship. The temperature of the determinations is not stated (but was most likely at room temperature) and no other details of these studies are currently available. These values are significantly higher than those in other studies, but compare with the values estimated from water solubility and vapour pressure given above (e.g. a dimensionless Henry's law constant of 500 at around 25°C is equivalent to a value of 1,239,000 Pa m^3/mol).

Another report by Xu *et al*. (2007) recommends a value for the dimensionless Henry's law constant (K_{aw}) for D4 of 490 (reported as log K_{aw} = 2.69) at 25°C. This is based on an as yet

unavailable study by Xu and Kropscott (2007) and is presumably related to the above results by Xu and Kozerski. This value is equivalent to a Henry's law constant of 1,214,000 Pa m^3/mol at 25°C.

From the available data on Henry's law constant, it is apparent that the measured values are significantly lower than that predicted on the basis of water solubility and vapour pressure alone, although the new determination by Xu and Kozerski (2007) is slightly higher than this predicted value. This implies inconsistency in these measured parameters and, therefore, some uncertainty in one or more of these parameters. However, the prediction of Henry's law constant from water solubility and vapour pressure is dependent on the substance showing ideal behaviour in solution; from the available data it is possible that this is not the case for D4. Therefore the Henry's law constants determined directly by experiment are considered in the assessment.

Although few details of the recent determinations of the Henry's law constant by Xu and Kropscott (2007) and Xu and Kozerski (2007) are currently available, this study was carried out by industry on a voluntary basis to address some of the uncertainties in this risk assessment. It is understood that the methodologies used were designed to avoid the potential problems of testing D4. Therefore, although currently it is not possible to validate these results fully, the value for the Henry's law constant for D4 is taken to be 1,214,000 Pa m^3/mol at 25°C [K_{aw} of 490 (log K_{aw} = 2.69)] based on the results of the study by Xu and Kropscott (2007). This value is self-consistent with the other partition coefficients used for D4.[5]

To assess the sensitivity of the assessment to the Henry's law constant, and to reflect the uncertainty in the determination of this parameter, the effect of using a lower Henry's law constant of 60,060 Pa m^3/mol at 28°C (equivalent to a dimensionless value of 24) on the conclusions of the assessment were also considered, based on the work of Kochetkov *et al*. (2001). This sensitivity analysis is reported in Appendix A.

1.3.9.4 Octanol–air partition coefficient

Very recently, the results of a study to investigate the octanol–air partition coefficient (K_{oa}) of D4 became available (Xu, 2006). The study was carried out using a mixture of ^{14}C-labelled D4 (^{14}C-D4), D5 (^{14}C-D5), and D6 (^{14}C-D6), and the D4 used was 99.2 per cent pure. The tests were carried out using gas syringes. Mixtures of the test substances in *n*-octanol were prepared [D4 concentrations between 0.3 and 30 ppm (mg/l) were tested; two concentrations were used for each temperature] and around 1–5 ml of this solution was added to 100 ml gas syringes. The syringes were incubated at –4°C, 5°C, 24°C, and 40°C. After equilibration for one hour, both the gas and octanol phases were analysed for D4. The mean log K_{oa} values for D4 were 5.08 at –4°C, 4.79 at 5°C, 4.22 at 24°C, and 3.92 at 40°C. The temperature dependence of the log K_{oa} value was fitted to Equation (1.3):

$$\log K_{oa} = A + B/T \qquad (1.3)$$

where A and B are constants (B is related to the internal energy change for D4 evaporating from the octanol to the air) and T is the absolute temperature (K).

The heat of evaporation (ΔU) was calculated from the B value to be 44.0 kJ/mol for D4.

Other values for the K_{oa} were reported in a poster presentation by Xu and Kozerski (2007). This reports measured log K_{oa} values of 4.46 for dry octanol and 4.30 using wet octanol. The

[5]For example, using the log K_{oa} of 4.34 at 25°C (see Section 0) and the log K_{ow} of 6.49 (see Section 1.3.7), a value for the log K_{aw} of 2.15 can be estimated. This compares well with the log K_{aw} of 2.69 used in the assessment.

temperature of the determinations was not stated and no further experimental details are available. It is possible that these values relate to the above study by Xu (2006) in which a similar log K_{oa} of 4.22 was determined at 24°C. Xu and Kozerski (2007) also calculated values for the log K_{oa} using linear solvation energy relationships. The values for D4 predicted using this method are 4.53 for dry octanol and 4.35 for wet octanol. Few other details of these calculations are currently available.

Xu *et al*. (2007) recommend a log K_{oa} value for D4 of 4.34 at 25°C. This is presumably based on the above study and calculated to 25°C. This value is considered in this risk assessment when appropriate.

1.3.9.5 Summary of physicochemical properties

The physicochemical properties of D4 are summarised in table 1.1.

Table 1.1 Summary of physicochemical properties

Property	Value used in risk assessment	Alternative value used in sensitivity analysis
Melting point	17.7°C	
Boiling point	175°C	
Density	0.95 g/cm^3 at 25°C	
Vapour pressure	132 Pa at 25°C	
Water solubility	0.056 mg/l at 23°C	
Log K_{ow}	6.49	5.1
Henry's law constant	1,214,000 Pa m^3/mol at 25°C	60,060 Pa m^3/mol at 28°C
Log K_{oa}	4.34 at 25°C	
Conversion factor for air	1 ppm = 12.1 mg/m^3 at 25°C	

Notes: [1]These values became available late in the risk-assessment process. The effects of these values on the conclusions of the risk assessment are considered in Appendix A.

2 General information on exposure

2.1 General introduction to the silicone industry

Although this report is concerned only with the non-polymeric cyclic organosiloxanes, in particular D4, to evaluate the potential for release to the environment it is necessary to understand the full life-cycle of products made from the substance of interest. This is particularly important in this instance, as a major use of D4 is as a monomer in the manufacture of polymeric materials. Such polymers could contain residual amounts of D4 (and, in some cases, could possibly break down to form small amounts of D4) and so the uses of the polymeric materials could, in some cases, act as sources of release to the environment of D4.

Therefore this section provides a general overview of the silicone industry relevant to the cyclic organosiloxanes. The specific uses of D4 itself are considered in more detail in Section 2.2.

Chandra (1997) reviews the commercially significant organosilicon materials produced worldwide. The review is based to a large extent on information from the United States of America (USA), but the review indicates that the industry in the USA is broadly similar to that in the European Union (EU) and Japan. The review provides useful background information for this project, and the main findings are summarised below. The information in the Chandra (1997) review is supplemented with information from other relevant sources.

Chandra (1997) considered five basic groups of organosiloxanes (also known as silicones), which are outlined in the sections below.

2.1.1 Oligomeric organosiloxanes

This group covers both cyclic and linear substances. The general formulae for oligomeric organosiloxanes are (Chandra, 1997):

- (R2SiO)x are cyclic substances, in which R is usually a methyl group, but can also be hydrogen, vinyl group, phenyl group, or a trifluoropropyl (CF3CH2CH2–) group, and x = 3, 4, 5, 6, etc (D4 falls into this group):
- R3SiO(SiR2O)nSiR3 are linear substances in which R is usually a methyl group, but can also be a phenyl group, and n = 0, 1, 2, 3, 4, etc.

The linear products are manufactured by the stoichiometric co-hydrolysis of two chlorosilanes (Chandra, 1997). An example reaction scheme is:

$$2(CH_3)_3SiCl + (CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3 + 4HCl$$

Hydrogen chloride is recovered and the products are purified by distillation.

The cyclic products are formed by the hydrolysis of dimethyldichlorosilane. Oligomeric siloxanols are formed as a by-product (the mixture of cyclic products and oligomeric siloxanols is often called hydrolysate):

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow [(CH_3)_2Si(OH)_2] + 2HCl \rightarrow [(CH_3)_2SiO]_x + HO[Si(CH_3)_2O]_yH$$

where the products are cyclic siloxanes (x = 3, 4, 5, 6, etc.) and oligomeric siloxanols (y = 2, 3, 4, etc.).

The value of x and y, and the ratio of linear to cyclic products, depends on the hydrolysis conditions used, for example the amount of water, the acidity, and the use of solvents (Chandra, 1997).

The hydrolysis of dimethyldichlorosilane is carried out commercially using either a batch or a continuous process (Rich *et al.*, 1997). In a typical process, the dimethyldichlorosilane is mixed with 22 per cent aqueous hydrochloric acid in a continuous reactor. The hydrolysate and concentrated hydrochloric acid are then separated in a decanter and the hydrogen chloride converted into methyl chloride (a starting material in the production of dimethyldichlorosilane). The hydrolysate is then washed to remove residual acid, neutralised, dried, and filtered. The water from the washing and neutralisation procedure is treated in an on-site wastewater treatment plant (WWTP) or is reused in the hydrolysis process. The typical yield of cyclic oligomers is between 35 and 50 per cent, and consists mainly of D4 and D5.

The complete conversion of dimethyldichlorosilane into linear silanols is possible using a continuous hydrolysis process, in which the cyclic products are separated from the linear oligomers by a stripping process and re-introduced into the hydrolysis process with the dimethyldichlorosilane starting material (Rich *et al*., 1997). Linear silanols can also be produced by methanolysis of dimethyldichlorosilane.

The cyclic products may be separated and purified by distillation (Chandra, 1997).

Very pure (>99.99 per cent) dimethyldichlorosilane starting material is needed if the linear fraction of siloxane oligomers is to be used directly in the manufacture of silicone polymers (Rich *et al.*, 1997). Methyltrichlorosilane impurity in the starting material can produce significant amounts of trifunctional units in the resulting oligomers, which may adversely affect the properties of the final polymeric products. If high-purity dimethyldichlorosilane is not used, an additional cracking step must be included in the overall production process. In the cracking step, the hydrolysate is depolymerised in the presence of strong bases or acids to give cyclic monomers, such as D4 and D5, which are removed by distillation. The trifunctional by-products remain in the reaction medium and are periodically removed.

As a group, the oligomeric organosiloxanes are also known as volatile methylsiloxanes (VMSs).

Around 87 per cent of the VMSs produced in the USA in 1993 were used as site-limited intermediates for the production of polymeric siloxanes (Chandra, 1997). The remaining 13 per cent (amounting to around 20,000 tonnes) were used in personal care products (particularly the D4 and D5 cyclic products). The primary uses in personal care products were as carriers in antiperspirants, deodorants, skin care products, and as conditioners for hair care products.

The Cosmetic Toiletry and Perfumery Association (CTPA) indicate that the functions of the cyclic siloxanes used in cosmetics in the United Kingdom (UK) are, in general, in the following three main areas (CTPA, personal communication):

- as hair-conditioning agents
- as skin-conditioning agents (emollient)
- as solvents.

The types of products in which they are reported to be used include aftershave lotions, colognes, toilet waters, perfumery products, baby lotions, oils, powders and creams, baby shampoos, bath oils and bath salts, etc., make-up products, make-up removers and skin-cleaning products, deodorants and antiperspirants, eye creams and eye make-up products (such as powders, mascaras, pencils, etc.), general make-up (such as foundations, blushers, face powders, and lipsticks), shampoos, conditioners, and hair dyes and colours, hair sprays, shaving products, skin-care preparations (such as creams, lotions, cleansers, and toners), sun creams and after-sun products, and hair-grooming aids.

2.1.2 Polymeric dimethylsiloxanes

More that 80 per cent of commercial organosilicon products are based on polydimethylsiloxane (PDMS) (Chandra, 1997). The general structures are:

$$(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$$

or

$$HO[Si(CH_3)_2O]_nH$$

where n = 5–6000 or more.

The starting material for the manufacture of PDMS is dimethyldichlorosilane. The first step in the process is hydrolysis to form cyclic siloxanes and/or linear siloxanols according to the reactions outlined in Section 2.1.1. PDMS itself is then formed by either the ring-opening polymerisation of cyclic siloxanes or the polycondensation of linear siloxanols in the presence of an endblocker, such as $[(CH_3)_3Si]_2O$ and heat under acid or alkaline conditions (Chandra, 1997). Example reactions are summarised as:

$$n/4[(CH_3)_2SiO]_4 + [(CH_3)_3Si]_2O \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$$

$$HO[Si(CH_3)_2O]_nH + [(CH_3)_3Si]_2O \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$$

The ratio of the endblocker to $–Si(CH_3)_2O–$ units in the starting material effectively determines the degree of polymerisation (n). The absence of any branching or cross-linking units (which arise from the processing conditions and/or impurities in the starting materials) is important when manufacturing PDMS with a high degree of polymerisation, i.e. with a long chain length (Chandra, 1997).

For the ring-opening polymerisation process, the commercially most important cyclic monomer used is D4 (Rich *et al.*, 1997), but other cyclic monomers, such as D5 and D6, are also used. The process can be carried out under anionic (basic) or cationic (acidic) conditions or in aqueous emulsions. The anionic polymerisation can be conducted in a batch reactor or in a continuously stirred reactor. The viscosity of the polymer and the type of end group can be easily controlled by the amounts of water and triorganosilyl chain-terminating groups added. A plasma polymerisation process was also developed for applications in

which a well-defined, thin polymer film is needed, such as in optics, electronics, or biomedicine.

Both the polycondensation and, in particular, the ring-opening polymerisation process can result in the formation of a mixture of high molecular weight polymer and low molecular weight cyclic oligomers, as the reactions are effectively equilibrium reactions (Rich *et al.*, 1997). For the ring-opening polymerisation process, the position of the equilibrium depends on the nature of the substituents on silicon and on the concentration of the siloxane units, but it is independent of the starting siloxane composition and the polymerisation conditions. The equilibrium concentration of cyclosiloxanes is thought to be around 18 per cent by weight and is thought to consist of a continuous population to at least D400, but with D4, D5, and D6 making up >95 per cent of the total cyclic fraction.

Low viscosity ($<10^5$ mm^2/s) PDMS-based fluids are usually prepared by an acid-catalysed process, using either a continuous process or glass-lined batch reactors, at temperatures up to 180°C (Rich *et al.*, 1997). After reaction the fluids are filtered and the residual low molecular weight cyclic and linear siloxanes removed by stripping under vacuum at elevated temperature.

High viscosity ($>10^6$ mm^2/s; high molecular weight) PDMS-based fluids (oils and gums) are usually prepared by base-catalysed, ring-opening polymerisation of hexamethylcyclotrisiloxane (D3) or D4 or by condensation polymerisation of silanol-terminated PDMS. Potassium silanoate or transient catalysts, such as tetramethylammonium hydroxide or tetrabutylphosphonium hydroxide, are used in the ring-opening process. The transient catalysts are destroyed at temperatures >150°C.

Around 138,000 tonnes of PDMS was produced in or imported into the USA in 1993 (Chandra, 1997). Around 62 per cent of this was used as site-limited intermediates in the production of elastomers, pressure-sensitive adhesives, and modified PDMS fluids (see below).

The non-intermediate industrial uses of PDMS are numerous (Chandra, 1997). Industrial uses in the USA include antifoams, softness and wetting agents in textile manufacturing, components of polishes and other surface-treatment formulations, lubricants, mould-release agents, paper coatings, and as dielectric fluids and heat-transfer liquids. PDMS is also used in consumer applications such as personal, household and automotive care products.

Ashford (1994) also indicates numerous uses for PDMS, such as:

- a foaming agent in oil processing;
- a flow and/or gloss improver in alkyd paints and varnishes;
- a lubricant in polishes and maintenance products;
- in anti-adhesion coatings;
- in hydraulic, dielectric, and heat-transfer fluids and in diffusion pump oils;
- in barrier creams and lipsticks, and in pharmaceuticals;
- in lubricants for motors, instruments, and precision bearings;
- in silicone emulsions used as antifoams;
- in anti-adherence coatings;
- in mould-release agents;

- in textile waterproofing;
- in silicone greases for gear and bearing lubrications;
- in silicone pastes for valve lubricants, mould-release agents, and electrical and electronic protection;
- as an additive in textile and paper sizing.

Silicone oils are stable over a wide temperature range (Rich *et al.*, 1997). The inclusion of diphenyl- or phenylmethylsiloxy groups into the polymer (see modified PDMS, Section 2.1.3) reduces the pour point of the fluid and increases the temperature stability. Methylsilicone oils are stable in air at 150°C for long periods of time, and undergo only slow degradation at temperatures up to 200°C. Increasing the amounts of phenyl-containing substituents increases the heat resistance and, for example, high molecular weight methylphenylsilicones can be used in air at up to 250°C for several hours. Stabilisers such as *p*-aminophenol, naphthols, metal acetonylacetonates, and iron octoate can be used to improve the thermal stability further.

When heated, PDMS fluids decompose by two main mechanisms (Rich *et al.*, 1997). At temperatures above 140°C retrocyclisation into volatile cyclic siloxanes, such as D3 and D4, can occur. The decomposition is catalysed by acids and bases. At 200–250°C thermal oxidation can occur and lead to the formation of formaldehyde, carbon dioxide (CO_2), water, and alkylsilicones.

PDMS is approved for food use in the UK (known as E900).[6]

Based on the above discussion PDMS products may contain a range of cyclic siloxanes which may be present in small amounts as impurities (particularly D4, D5, and D6; see Section 0). Furthermore, under certain conditions (elevated temperatures in the presence of acidic and basic catalysts) PDMS products may decompose to form small amounts of cyclic siloxanes. Therefore the uses of PDMS are potentially relevant to the life cycle of D4.

2.1.3 Modified polymeric dimethylsiloxanes

Also available is a range of modified PDMSs in which some of the methyl groups are replaced by other groups (Chandra, 1997). These have the general formulae.

$$(CH_3)_3SiO(SiX(CH_3)O)_m[Si(CH_3)_2O]_nSi(CH_3)_3$$

or

$$X(CH_3)_2SiO[Si(CH_3)O]_2[Si(CH_3)_2O]_nSi(CH_3)_2X$$

where X = H, alkyl, vinyl, phenyl, $CF_3CH_2CH_2$–, aminoalkyl, or epoxyalkyl.

Modified PDMS is commonly manufactured by the catalysed ring-opening copolymerisation of an appropriate functional monomer (either cyclic or linear) with a cyclic oligomeric siloxane and an endblocker such as $[(CH_3)_3Si]_2O$. Example reaction schemes are:

$$[(CH_3)_2SiO]_x + [X(CH_3)SiO]_y + [(CH_3)_3Si]_2O \rightarrow (CH)_3SiO[Si(CH_3)_2O]_x[SiX(CH_3)O]_ySi(CH_3)_3$$

cyclic cyclic linear

or

[6]See http://www.food.gov.uk/safereating/additivesbranch/enumberlist.

$[(CH_3)_2SiO]_x + [X(CH_3)_2Si]_2O + \rightarrow X(CH_3)_2SiO[Si(CH_3)_2O]_xSi(CH_3)_2X$

cyclic linear

where X = H, alkyl, vinyl, phenyl, $CF_3CH_2CH_2$–, aminoalkyl, or epoxyalkyl.

The cyclic and linear functional monomers are made (sometimes *in situ*) from the corresponding alkoxysilanes according to the processes:

$y[X(CH_3)Si(OR)_2] + yH_2O \rightarrow [X(CH_3)SiO]_y + 2y\text{ROH}$

cyclic

or

$2X(CH_3)_2SiOR + H_2O \rightarrow [X(CH_3)_2Si]_2O + 2\text{ROH}$

linear

Other methods for synthesis of modified PDMS are by the hydrosilylation reaction or by nucleophilic substitution reactions.

The most significant modified PDMS fluids, on a commercial basis, include the methyl(hydrido)siloxanes, methyl(vinyl)siloxanes, methyl(alkyl)siloxanes, methyl(phenyl)siloxanes, methyl(trifluoropropyl)siloxanes, and methyl(aminoalkyl)siloxanes (Chandra, 1997).

The methyl(hydrido)- and methyl(vinyl)siloxanes contain reactive sites for cross-linking in the production of silicone elastomers (see Section 2.1.5). The methyl(hydrido)siloxanes are also used as intermediates and as waterproofing agents for textiles and wall boards.

The methyl(phenyl)siloxanes are used as high-temperature oil baths, greases, diffusion pump fluids, and paint additives.

The trifluoropropyl group gives greater solvent and fuel resistance to the silicone rubber for use in, for example, gasket materials.

The methyl(alkyl)siloxanes are used as release agents for plastics and urethane parts, for cutting oils, and as paint additives.

The methyl(aminoalkyl)siloxanes are used in a wide range of applications, such as textiles, personal care products, household care products, automotive care products, and in plastic modification (the aminoalkyl group acts as a reactive site to give a permanent point of attachment).

Similar to the case with PDMS, modified PDMS polymer products may contain small amounts of cyclic siloxanes as impurities (the levels present are currently unclear). Therefore the uses of modified PDMS are potentially relevant to the life cycle of D4.

2.1.4 Organosiloxane resins

These resins are made from starting materials not covered by this assessment (i.e. trichlorosilanes and other silanes) and so are not considered further.

2.1.5 Organosiloxane elastomers

Organosiloxane (silicone) elastomers (rubbers) are used for coatings, gels, sealants, and rubbers (Chandra, 1997). They are cross-linked PDMS and in some trifluoropropyl or phenyl groups replace some of the methyl groups in the PDMS.

Many systems have been developed for cross-linking PDMS (curing and vulcanising). The curing systems can be broadly divided into three main types: peroxide cure, hydrosilylation or addition cure, and condensation cure (Rich *et al*., 1997). Other curing systems that can be used include high-energy radiation cure and photo-initiated radiation cure.

Peroxide curing systems work at elevated temperatures and use peroxides such as dibenzoyl peroxide, bis-*p*-chlorobenzoyl peroxide, bis-2,4-dichlorobenzoyl peroxide, dicumyl peroxide, di-*t*-butyl peroxide, and 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane (Rich *et al.*, 1997). The amount and type of peroxide used determines the cure temperature and overall properties of the final rubber. Vinyl-containing polymers are often used to control the cross-linking reaction.

The addition cure (hydrosilylation) system involves the reaction between a silicon hydride group and a vinyl group to form an ethylenic linkage (Rich *et al*., 1997). The reaction is catalysed by certain metals, such as platinum. Inhibitors can also be incorporated into the products to increase the storage life and cure temperature, and so allow the product to be more easily handling during use.

The condensation cure system involves the condensation of silanol groups in the polymer to form siloxanes (Rich *et al.*, 1997). Curing agents include alkoxysilanes, acyloxysilanes, silicon hydrides, and methylethyloximesilanes. Catalysts for the reactions include acids, bases, and organometallic compounds [(e.g. carboxylic acid complexes of tin(II) and tin(IV)].

Some formulations are supplied as one-part systems whereas others are supplied as two-part systems. Some products cure at room temperature [room temperature vulcanising (RTV)] while others are heat-cured -heat-activated vulcanising (HAV)].

A typical one-part cold-cured system is based on hydroxyl-terminated PDMS with methyl triacetoxysilane as the curing agent. Curing occurs by a condensation reaction in the presence of moisture, which releases acetic acid. Cold-cured two-part systems can be cured either by a condensation reaction or by an addition reaction. A condensation-cured two-part system is based on hydroxyl-terminated PDMS and ethyl silicate. An addition-cured two-part system is based on vinylated PDMS, PDMS, and a cross-linking agent. A heat-cured system is based on vinylated PDMS and fumed silica (Ashford, 1994).

Rich *et al.* (1997) indicate that most silicone rubbers contain additives, such as filler. Reinforcing fillers are used at concentrations of 10–25 per cent by weight to increase the tensile strength, tear strength, and abrasion resistance, and include finely divided silicas (prepared by vapour-phase hydrolysis or oxidation of chlorosilanes), dehydrated silica gels, precipitated silicas, diatomaceous silicas, and finely ground high-assay natural silicas. Non-reinforcing fillers are used to reduce the cost of the product and to improve heat stability, impart colour, and increase electrical conductivity. Non-reinforcing fillers include calcium carbonate, clays, silicates, aluminates, pigment-grade oxides (e.g. ferric oxide), fumed oxides of titanium, aluminium, and zirconium, and carbon black. Plasticity and process aids are also often added to aid subsequent processing. Rich *et al.* (1997) indicate that, as an alternative to aid subsequent processing, in some situations the silica particles used as fillers may be reacted with hot vapours of low molecular weight cyclic siloxanes and hexamethyldisiloxane prior to incorporation in the rubber.

RTV silicones cure on exposure to atmospheric oxygen – the rate of cure depends on the temperature and humidity (Rich *et al*., 1997). Uncured products have a shelf-life of six

months to several years. Two main curing systems are used, based on either acetoxy silicone compounds or alkoxy silicone compounds. Both work in essentially the same way, by reaction with the silanol group in silanol-terminated PDMS, which results in the formation of hydrolytically unstable acetoxy- or alkoxy- groups. These groups hydrolyse on exposure to moisture (releasing ether acetic acid or alcohols) and diol groups are formed at the end of the PDMS, which can then undergo condensation reactions (catalysts may be used to increase the rate of cure) and lead to formation of cured silicone rubber. The commercial uses of the acetoxy-based products are limited by the odour and corrosive nature of the acetic acid formed. One-part RTV silicone products find applications in household consumer products, construction products, and industrial adhesives.

Heat-cured silicone rubbers are processed using similar methods as those for natural rubber (Rich *et al.*, 1997). For example the high molecular weight PDMS polymer (often termed gum) and fillers are firstly compounded using a dough or Banbury-type mixer. Catalysts (curing agents) are then added and the rubber is further compounded on water-cooled roll mills. For small batches the entire process can be carried out on a two-roll mill.

Heat-cured silicone rubber is commercially available in a variety of compounded, semi-compounded, or uncompounded forms, for example gum stock, reinforced gum stock, partially filled gum, uncatalysed compounds, dispersions and catalysed compounds (Rich *et al.,* 1997*).* The rubber is frequently re-worked on a rubber mill prior to use (i.e. worked until it is a smooth continuous sheet).

The most common processing method for heat-cured silicone rubber is compression moulding at 100–180°C under pressure (5.5–10.3 MPa) using mould-release compounds (Rich *et al*., 1997). Under these conditions the rubber usually cures in a few minutes. Other processes that can be used include extrusion (for the manufacture of tubes, rods, wire and cable insulation, and continuous profile). Following extrusion the products are initially cured in hot air or steam tunnels at 300–450°C under reduced pressure (276–690 kPa) for several minutes. The products are then further cured (post-cured) in air or steam for a further 30-90 minutes.

To make coated textiles and glass cloth the gum stock is dissolved in solvent and the rubber applied by dip coating (Rich *et al*., 1997). After drying the coating is cured in heated towers. The treated textiles can be used to form tubes and hoses of complex shapes.

Silicone rubber made from a low-viscosity starting material can be processed by liquid–injection moulding (Rich *et al*., 1997). In this process the rubber is injected into moulds similar to those used for plastic injection moulding and cured within the mould. This process allows complex shapes to be moulded. In the system the rubber is rapidly cured (in 10–40 seconds) using a low moulding pressure (2–20 MPa) at temperatures of 150–260°C. The process is used for applications such as electrical connectors, O-ring seals, valves, electrical components, health care products, and sports equipment (goggles and scuba masks).

The rubber used for liquid-injection moulding is usually a two part system (Rich *et al*., 1997). One part of the system (Part A) contains a linear dimethylsiloxane polymer with terminal and pendent vinyl groups, fillers, a hydrosilylation (addition) catalyst (e.g. platinum), and a catalyst inhibitor. The second part (Part B) contains a linear dimethylsiloxane polymer with pendent Si-H groups, fillers, pigments, and stabilisers. One-part systems, in which the hydrosilylation catalyst is deactivated at room temperature (it reactivates when heated to >100°C), have also been developed.

Foamed or sponge silicone rubber products can also be manufactured by incorporating suitable blowing agents into the rubber stock (Rich *et al.*, 1997). The polymer systems used are generally similar to the two-part systems used in liquid-injection moulding, but one part also contains water, alcohol, and an emulsifying agent. The two parts are mixed at room

temperature, which initiates the cross-linking reaction and also results in the formation of hydrogen gas (from the platinum-catalysed reaction of the hydroxyl groups from the water and/or alcohol with the Si–H groups), which acts as the blowing agent. The typical time for foam formation is around 20 minutes. Silicone foam, particularly when quartz is used as filler, has good flammability characteristics and so is used in building and construction fire-stop systems and as pipe insulation in power plants.

Primers (such as silicate or titanate esters from the hydrolysis of tetra-ethylorthosilicate or tetra-ethyltitanate) are used when silicone rubber is to be bonded onto surfaces, such as those of metals, plastics, or ceramics (Rich *et al*., 1997).

Organic solvent can diffuse into silicone rubber and significantly decrease the physical properties of the rubber (Rich *et al.*, 1997). For applications in which the material may be exposed to solvents, for example fuel-tank sealants, solvent-resistant rubber based on trifluoropropylmethylsiloxane (or β-cyanoethylmethylsiloxane, although these are of much less importance commercially) polymers are available.

Pure water has little effect on the properties of silicone rubber, but prolonged exposure to aqueous acids or bases can cause degradation of the rubber to a sticky gum (Rich *et al.*, 1997).

Around 89,000 tonnes of silicone elastomers were produced or imported in the USA in 1993 (Chandra, 1997). Applications of RTV products include sealants, encapsulants, foams, coatings, caulking, and mould making. Applications of heat-cured rubber include tubing, hoses, wire and cable insulation, penetration seals, laminates, release coatings, foams, and other moulded and extruded articles, such as gaskets, key pads, ignition cables, belting, and catheters. Gel applications include electronic encapsulates and wound-dressing patches.

Ashford (1994) lists many possible uses for silicone rubbers (elastomers). One component cold-cured rubbers are used as caulks and sealants for expansion joints and windows, for seals, gaskets, and shock-absorbing fixing in vehicles and domestic appliances, and in heat-resistant adhesives. Two component cold-cured (addition cured) rubbers are used as dielectric gels, for electronic and electrical encapsulation, in fire-resistant cable coatings, in foamed sealants, and in resin-casting moulds. Two-component cold-cured (condensation cured) rubbers are used as moulding compounds for furniture and construction, in paper anti-adhesion coatings, as electrical component sealants, as roofing membranes, and as window and curtain walling sealants. Heat-cured silicone rubbers are used in chemical resistant and medical tubing and mouldings, flexible and rigid foams, press-foamed automobile seals, and wire and cable jacketing.

Rich *et al.*, (1997) indicate that a growing area of use of thermally cured silicones is in paper-release coatings used in label systems. The silicone coating forms part of the disposable liner and is applied to substrates such as supercalendered kraft paper, glassines, and thermally sensitive films, such as polyethylene and polypropylene. The coatings are usually based on solvent-free mixtures of PDMS with terminal vinyl groups, a cross-linking agent that contains Si–H groups, a hydrosilylation catalyst (typically platinum), and a cure inhibitor. MQ resins [clusters of quadrafunctional silicate groups (Q) end-capped with monofunctional trimethylsiloxy groups (M)] may also be incorporated as control-release additives. Curing is carried out at 150°C or lower and line speeds of up to 460 m/minute can be achieved. Also, the industry is evolving towards using products that can be cured by ultraviolet (UV) light.

Similar to the case with PDMS, silicone elastomers may contain small residual quantities of cyclic siloxanes and so the uses of silicone elastomers are relevant to the life cycle of D4.

2.1.6 Consumption of silicones

The Centre Européen des Silicones (CES) published figures on the total worldwide consumption of silicones in 2002.[7] The total worldwide production in 2002 was 2,000,000 tonnes, with 33 per cent (~660,000 tonnes) used in Western Europe, 34 per cent (680,000 tonnes) in North America, 28 per cent (560,000 tonnes) in Asia, and 5 per cent (100,000 tonnes) in the rest of the world. Lassen *et al.* (2005) report a smaller consumption of silicones in 2002 in Western Europe of 296,000 tonnes/year. The breakdown of the total use between the various main applications in Western Europe in 2002 was:

- sealants, 210,000 tonnes (~32 per cent)
- elastomers, 139,000 tonnes (~21 per cent)
- fluids, 139,000 tonnes (~21 per cent)
- specialities, 92,000 tonnes (~14 per cent)
- silanes, 60,000 tonnes (~9 per cent)
- resins, 20,000 tonnes (~3 per cent).

A further, more detailed, breakdown was given for the Western European use of elastomers and silicone fluids. For elastomers, 20 per cent were used in automotive applications, 15 per cent in electrical fittings, 14 per cent in medical and healthcare applications, 9 per cent in appliances, 9 per cent in consumer goods, 7 per cent in textile coatings, 7 per cent in paints and coatings, 7 per cent in mould making, 5 per cent in business machines, and 7 per cent in other applications.

For the silicone fluids, 26 per cent were used as processing aids, 18 per cent were used in personal care products, 15 per cent were used in paper coatings, 10 per cent were used in paints and coatings, 7 per cent were used as mechanical fluids, 5 per cent were used in textile applications and 24 per cent were used in other applications.

2.2 Production of cyclic siloxanes in the EU

Four companies produce or supply D4 in the EU, and a manufacturing site exists in the UK. The actual quantities produced at the various sites are confidential. The information available is summarised in a confidential annex to this report.

2.3 Uses

The uses of D4 can be divided into four main areas:

- as a site-limited chemical intermediate at the site of production;
- as an off-site chemical intermediate;
- in personal care products (e.g. cosmetic products, and skin- and hair-care products);

[7] See http://www.silicones-europe.com/ab_facts.html.

- in household products (e.g. cleaning products).

CES provided information on the amounts of D4 supplied in the EU and the UK. Some of these figures are confidential and are summarised in the confidential annex to this report. The non-confidential figures for D4 are summarised in table 2.1

Table 2.1 Uses of D4 in the UK and Europe

Life-cycle step	Amount used in Europe (tonnes/year)		Amount used in UK (tonnes/year)	
	2003	**2004**	**2003**	**2004**
Chemical intermediate – internal	Confidential	Confidential	Confidential	Confidential
Chemical intermediate – external – polymers	5771 [1]	8866 [1]	3.5	20
Chemical intermediate – external – silica	Confidential	Confidential	Confidential	Confidential
Personal care	892	579	353	107
Household products	Confidential	Confidential	Confidential	Confidential
Other and unspecified	Confidential	Confidential	Confidential	Confidential
Total	**Confidential**	**Confidential**	**Confidential**	**Confidential**

Notes: [1]The figures for the chemical intermediate – external were provided in a subsequent survey of CES Members and downstream users (CES, 2005b).

Lassen *et al.* (2005) report that D4 is registered in 49 product types in the Danish Product Register. These product types included paints, cleaning agents, dyes, fillers, polishes, and adhesives, among others (it is not, however, always clear if these product types are relevant to D4 specifically or siloxanes in general). In most product groups the total registered amount is small. The main uses of D4 in Denmark appear to be in personal care products. Similarly, the Nordic SPIN database gives several uses of D4, including fuel additives, cleaning and washing agents, impregnation materials, adhesives, binding agents, surface treatment, construction materials, paints, lacquers and varnishes, fillers, reprographic agents, process regulators and anti-set-off agents, anti-adhesive agents, and cosmetics (TemaNord, 2005). Environment Canada (2008) indicates that in Canada there may be some use of D4 in waxes and polishes (D4 content between 1 and 5 per cent) and in surfactants and defoamers (D4 content between 1 and 100 per cent). Some of these uses are not confirmed for the UK in the CES survey and so are not considered further here. It is possible that these may refer to uses of PDMSs made from D4 rather than direct use of D4.

2.4 Life cycle

The overall life cycle of the various silicone products relevant to this project is summarised in Figure 2.1

Figure 2.1 Western European usage of silicones

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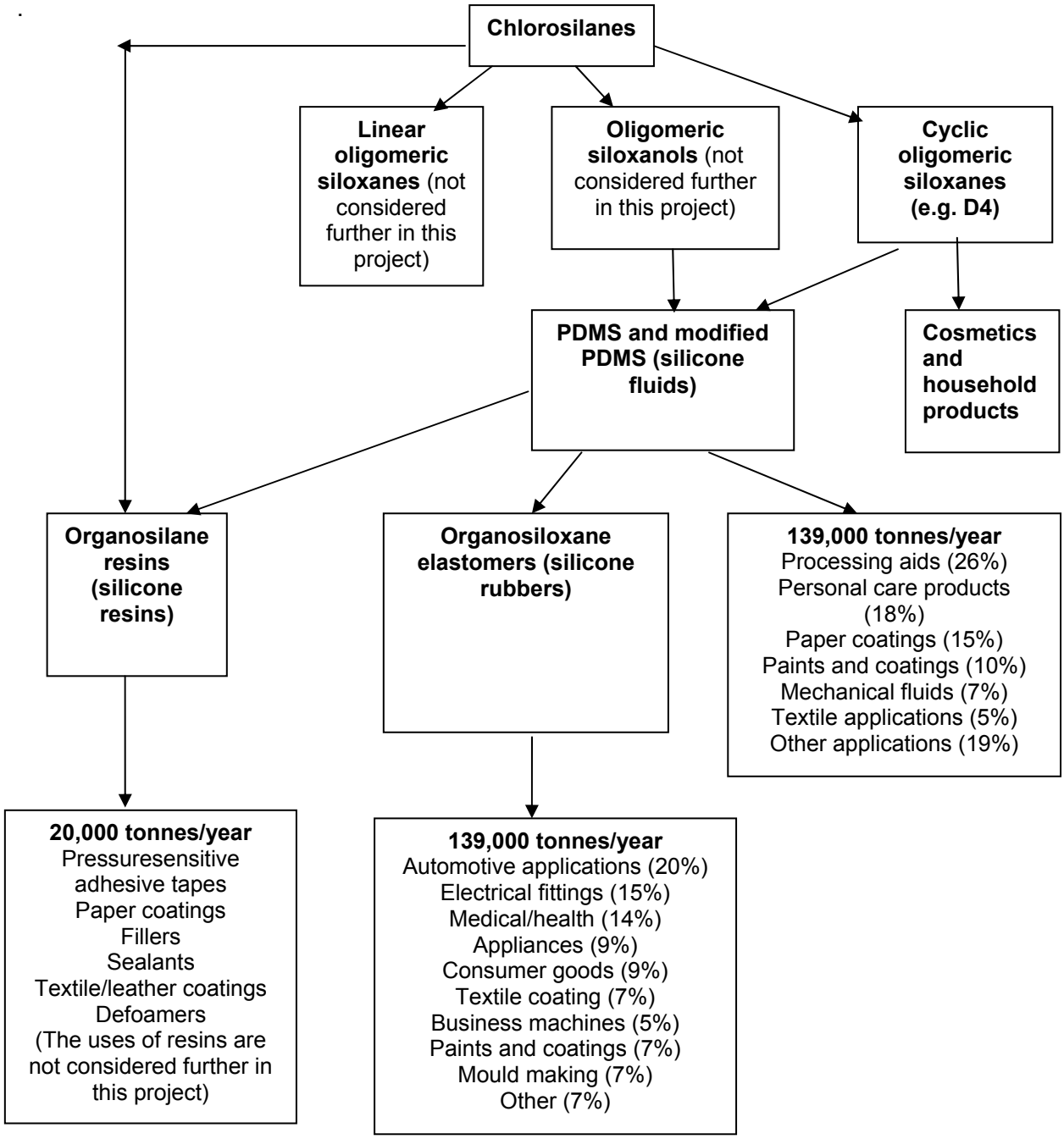

2.5 Trends

Based on the confidential information provided for this assessment, the production of D4 in the UK shows an increasing trend over recent years, but the use in personal care products and household products shows a generally decreasing trend in both the UK and the EU. However, this analysis is based on relatively few data points (in some cases only two years).

2.6 Legislative controls

In Germany, an air-emission standard (TA Luft Grenzwert) applies to D4 (CES, 2005b). The maximum permitted emission limit is 0.5 kg/h or 100 mg/m^3. There is also a standard for internal air Niedrigste Interessierende Konzentration (NIK) for D4. This value is set at 1.2 mg/m^3.

In the Netherlands, a maximum permissible concentration (MPC) of 0.44 µg/l is used for D4 in work performed within the framework of EU Directive 76/464/EEC (Plassche *et al.*, 1999). This value is calculated on the basis of the lowest no observed effect concentration (NOEC) from an early life-stage study with *Oncorhynchus mykiss* (>4.4 µg/l) and an assessment factor (AF) of ten applied. For the sediment compartment, the derived MPC was 2.0 mg/kg dry weight based on the geometric mean NOEC from the study with *Chironomus tentans* (198 mg/kg dry weight, normalised to a standard sediment with a 10 per cent organic matter content) and an AF of 100 applied. The MPC for standard soil was calculated as 1.3 mg/kg dry weight using the equilibrium partitioning method.

In the USA, VMSs, including D4, are exempt from volatile organic compound (VOC) legislation because laboratory experiments at the University of California demonstrated that, in contrast to certain other organic compounds of similar reactivity, the breakdown of VMSs in the atmosphere does not lead to the formation of ground-level ozone (CES, 2005b). This work is also substantiated by Harwell Laboratory in the UK. Using computer modelling, the photochemical ozone creation potentials (POCPs) for a number of VMSs were calculated under European atmospheric conditions. It was concluded that the POCP value for D4 is close to zero.

3 Environmental Exposure

3.1 Environmental releases

In this assessment, releases to the environment are considered in various scenarios. The background to these is explained more fully in the Technical Guidance Document (TGD). The local environment is considered to be the environment near to a site of release (e.g. a production, formulation, or processing site). The regional environment is taken to represent a highly industrialised area. The continental environment is the size of the EU and is generally used to obtain 'background' concentrations of the substance.
A preliminary worst case estimate of the emissions was carried out using the A and B Tables from Appendix I of the TGDTGD. According to the TGD, the B Tables, which are used to define the size of the local site, should be applied to the total EU volume of the substance used unless there are indications that it is used at numerous sites, in which case the regional volume (10 per cent of the total EU volume) should be used. This is known as the 10 per cent rule. For D4 information is available on both the total EU volume and the volume used in the UK, and so, wherever appropriate, the B Tables for the UK volume are used to estimate the representative sizes for the sites in the UK where appropriate.
The regional releases are taken as 10 per cent of the total EU release, unless the release from a single site accounts for >10 per cent of the total EU release.
The emission estimates are based on the 2004 production and use figures where available.
The predicted environmental concentrations (PECs) are calculated using the European Union System for the Evaluation of Substances (EUSES) 2.0.3 program, which implements the methods given in the TGD.

3.1.1 Production and use as a chemical intermediate on-site

3.1.1.1 Default release estimate

The emissions from the UK production site can be estimated using the A and B Tables from the TGD. The relevant emission factors (taken from Table A1.1 or Table A2.2) for main category [(MC = 1c – (isolated intermediates stored off-site)] for D4 are:

- 0.001 (0.1 per cent) to air
- 0.003 (0.3 per cent) to wastewater.

3.1.1.2 Other emission data

Information is available on the amounts of D4 in various effluent streams at the production sites in the EU, and is summarised in Section 0. The data represent the emissions from the whole site and so include any on-site use of the substance as an intermediate.

Based on these figures, for D4 the emissions to water after waste treatment at the actual UK plant are of the order of 0.035–0.062 kg/day. These data are based on measurements taken around 2001. Using the 2001 production data for this site (confidential), an appropriate emission factor for D4 was derived and applied to the 2004 consumption data (details of the calculation are given in the confidential annex). This is used to estimate the current emission of D4 to water from the UK production site (after wastewater treatment) as 23.4 kg/year or 0.078 kg/day.

3.1.1.4 Summary of emissions used in preliminary assessment

For the preliminary assessment, the emissions to water estimated in Section are used, along with the default emissions estimated for air (see Section 0). The emissions to water are based on relatively few measurements and so are themselves uncertain, but even so it is clear from the limited data available that the actual emissions to water from the site are much lower than would be predicted from the default values.

The local emission estimates for D4 used in this assessment: are

- confidential to air
- 23.4 kg/year or 0.078 kg/day to surface water.

The number of days of emission is 300.

In addition the PEC calculation also takes into account the information available on the size of the WWTP [average flow 321 m^3/hour (0.089 m^3/s); 95th percentile high flow 499 m^3/hour (0.14 m^3/s)] and the flow of the receiving water (mean flow 0.225 m^3/s; 95th percentile low flow 0.039 m^3/s). Based on the mean flow rates the average dilution factor at this site is 0.225/0.089 = 2.5. No dilution is expected based on the 95th percentile low flow of the river and the 95th percentile high flow of the effluent treatment plant.

3.1.2 Use as a chemical intermediate off-site

The relevant Industry Category (IC) for this use is IC = 3: Chemical Industry: Chemicals used in synthesis. The relevant Use Category (UC) is UC = 33 (Intermediates). The default emission factors for off-site use as an intermediate are given in Table A3.3 of the TGD. The appropriate emission factors for D4 (assuming MC = 3 as a default) are:

- 0.01 (1 per cent) to air
- 0.007 (0.7 per cent) to wastewater (wet process)
- 0 to wastewater (dry process).

Two main applications exist in the UK and EU:

- as an intermediate (monomer) in polymer synthesis;
- for the surface treatment of amorphous silica.

3.1.2.1 Intermediate for off-site polymer synthesis

CES (2005b) completed the analysis of a questionnaire that requested further details of D4 emissions to water from UK and EU sites where D4 is used as an intermediate for off-site polymer synthesis. This information is summarised in the confidential annex. In the survey, a ‘dry process’ is defined as a process that does not involve aqueous processing of D4 and therefore does not result in release of D4, to the aqueous effluent stream from the site. Thus, for sites that use a dry process a zero emission to wastewater is assumed.

For D4, more than 98 per cent of the total volume used off-site as a chemical intermediate to manufacture polymers in the EU does not result in emissions to the water compartment. The corresponding figure for the UK is 22.5 per cent, but this is skewed because the total amount used in the UK is very small, and is dominated by one site that uses a wet process.

The Conseil Européen de l'Industrie Chimique (CEFIC) contacted the UK site and the one other site in the EU that uses D4 in a wet process for further information, which is used to derive the emission estimates for D4 used as an intermediate in polymer synthesis in a wet process:

- local (UK):
  - 1.6 kg/day to air
  - 0.1 kg/day to wastewater;
- local (EU):
  - 10.8 kg/day to air
  - 5.6 × 10–5 kg/day to wastewater;
- total UK:
  - confidential to air
  - confidential to wastewater;
- regional:
  - confidential to air
  - confidential to wastewater;
- total EU:
  - confidential to air
  - confidential to wastewater.

The number of days of emission for the local site is confidential.

The emission estimates for D4 used as an intermediate in polymer synthesis in a dry process are:

- local (UK):
  - 130 kg/year or 10 kg/day to air
  - 0 kg/year to wastewater;
- local (EU):
  - 22,170 kg/year or 74 kg/day to air
  - 0 kg/year to wastewater;
- total UK:
  - 190 kg/year air
  - 0 kg/year to wastewater;
- regional:
  - confidential to air
  - 0 kg/year to wastewater;

- total EU:
  - confidential to air
  - 0 kg/year to wastewater.

The number of days of emission for the local site is 13 days (UK) and 300 (EU).

For the emissions to water from local sites, the known size of the WWTP or the known size of the receiving water will be taken into account. Where these are not known, the Technical Guidance Default values will be used. The Emission Scenario Document for chemicals used in synthesis (reaction intermediates) in the TGD recommends the use of an effluent flow rate of 10,000 m^3/day (0.12 m^3/s) from the WWTP and a dilution factor of 40 for such sites. These values will be assumed in the PEC calculations where site-specific data are missing.

3.1.2.2 Use in amorphous silica treatment

The treatment of amorphous silica with D4 is a dry process whereby the D4 is adsorbed onto the surface of the silica. In the process, D4 is delivered in closed vessels and handled in closed systems. Excess D4 is burnt on-site. Therefore there should be no emissions to wastewater from this process (although emissions to air could possibly occur, but these are likely to be minimal if the waste stream is burnt).

CES (2005b) obtained further information from a major manufacturer of treated silica, which indicates that D4 is used at a typical concentration of 3–8 per cent in the final treated silica. If an average of 5 per cent is used, one tonne of D4 results in the production of 20 tonnes of treated silica.

Assuming a dry process (zero emission to waste-water) and the default emission factor to air [0.01 (i.e. 1 per cent)] the emissions estimated for this use of D4 are:

- local:
  - 2 kg/day to air
  - 0 kg/year to wastewater;
- total UK:
  - confidential to air
  - 0 kg/year to wastewater;
- regional:
  - confidential to air
  - 0 kg/year to wastewater;
- total EU:
  - confidential to air
  - 0 kg/year to wastewater.

Further details of the calculations are given in the confidential annex. The number of days of emission for the local site is confidential.

3.1.3 Use in personal care products

The relevant IC and UC for this use are IC = 5: Personal/Domestic and UC = 15 (Cosmetics).

3.1.3.1 Formulation

The default emissions from formulation of personal care products can be estimated using Table A2.#[8] of the TGD. The relevant emission factors are:

- formulation of liquid products:
  - 0.00002 (0.002 per cent) to air
  - 0.0009 (0.09 per cent) to wastewater;
- others/unknown:
  - 0.0002 (0.02 per cent) to air
  - 0.0009 (0.09 per cent) to wastewater.

As D4 is used to make a range of products, both solids and liquids, the higher emission factor to air is used in the calculations as a worst case.

The worst-case amount formulated on a site and the number of days of formulation can be estimated using Table B2.3 of the TGD. This table applies to the total volume of cosmetics that contain D4 in a region.

The cyclic siloxane contents of cosmetic and skin-care products can vary widely, from a few percent to 90 per cent or more. Therefore to carry out a preliminary analysis here, a figure of around 30 per cent is used. Using this figure and the amount of D4 supplied to the personal care industry in the UK, the total amount of cosmetics and personal care products that are formulated in the UK and contain D4 can be estimated as 356 tonnes/year.

Using these figures in Table B2.3 gives the amount of cosmetic s and the amount of D5 formulated, on a worst-case local over 300 days, as 356 tonnes/year and 107 tonnes/year, respectively.

The Cosmetics, Toiletry and Perfumery Association (CTPA) surveyed 39 cosmetic formulation sites in the UK. The amounts of D4, D5, and cyclomethicone (a general term used for mixtures of D4, D5, and D6) used at the sites were determined. No use of any of these substances was reported at 21 of these sites. The amounts used at the other sites are confidential, but it is clear from the results of the survey that only one or two sites are of the size represented by the upper end of the consumption range, with many sites using much smaller volumes than this upper limit. Based on these data the appropriate size for a representative generic site is estimated at 3 tonnes/year of D4 over 300 days.

[8]This is how the Table is numbered in the TGD. The actual number is not clear.

Using this value and the above default emission factors, the emissions of D6 from formulation can be estimated:

- local, generic site:
  - 0.6 kg/year or 0.002 kg/day to air
  - 2.7 kg/year or 0.009 kg/day to wastewater;
- total UK emission:
  - 19 kg/year to air
  - 96 kg/year to wastewater;
- regional:
  - 10.3 kg/year to air
  - 51.0 kg/year to wastewater;
- total EU emission:
  - 103 kg/year to air
  - 510 kg/year to wastewater.

In addition, the CTPA survey allows us to estimate the release of D4 from sites that use it or cyclomethicone. These calculations are confidential, but the local releases in the UK are in the ranges 5.2×10^{-6} to 4.7×10^{-3} kg/day to air and 4.3×10^{-5} to 0.021 kg/day to wastewater.

The number of days of emission from the local site is 300 in all cases.

The estimates for UK sites that use D4 are considered in this assessment. The generic site can be used as a guide for possible releases from other sites within the EU.

3.1.3.2 Use by general public

The emissions to the environment through use by the general public are taken to be 90 per cent to air and 10 per cent to wastewater. This is based on the assumption that 100 per cent emission to air occur for products applied to the skin (e.g. skin creams, antiperspirants, etc.) and 100 per cent emission to wastewater occurs for hair-care products (that may be washed out immediately after application), along with an analysis of the relative proportion of these two types of products that contain cyclic siloxanes in the UK.

The amounts of D4 used to formulate personal care products in the EU and the UK are summarised in Section 2.3. However, the CTPA indicate that companies export a large amount of the products formulated in the UK to other parts of the EU and the world. The actual amounts of personal care products used in the UK that contain D4 are unknown, but as a first approximation the CTPA suggest that the UK market should be taken as 14.7 per cent of the old EU15 plus Norway and Switzerland.

Based on the UK market being 14.7 per cent of the total EU, the amounts of cosmetics that contain D4 (assuming a content of 30 per cent as before) and D4 itself used in the UK can therefore be estimated as 278 tonnes/year and 83 tonnes/year, respectively.

For the local assessment it is assumed that this tonnage is equally distributed about the UK. Using a UK population of 60 million, the average usage for each substance in personal care products can be estimated as 0.0014 kg/person/year.

Assuming a local site (in this case a WWTP) serves 10,000 inhabitants, and that 10 per cent of the products used are released to water and 90 per cent are released to air, the local release to such a plant can be estimated (release is assumed to occur over 365 days per year). The regional release is based on a population of 2×10^7 inhabitants, as recommended in the TGD. It is only relevant to consider the direct release to air from use of personal care products at regional and continental levels. The estimates for D4 are:

- local, 1.4 kg/year or 3.8 × 10–3 kg/day to wastewater;
- total UK:
  - 76,500 kg/year to air
  - 8500 kg/year to wastewater;
- regional:
  - 25,200 kg/year to air
  - 2800 kg/year to wastewater;
- total EU:
  - 510,300 kg/year to air
  - 56,700 kg/year to wastewater.

3.1.4 Household products

The relevant IC and UC for this use are IC = 5: Personal/Domestic and UC = 9 (Cleaning/washing agents).

3.1.4.1 Formulation

The default emissions from formulation of household products are estimated using Table A2.2 of the TGD. The relevant emission factors are:

- formulation of liquid products:
  - 0.00002 (0.002 per cent) to air
  - 0.0009 (0.09 per cent) to wastewater;
- others/unknown
  - 0.0002 (0.02 per cent) to air
  - 0.0009 (0.09 per cent) to wastewater.

Details of the calculation of the emissions using these values are confidential.

3.1.4.2 Use by general public

The default emissions to the environment from use of household products by the general public are estimated using Table A4.1. The relevant emission factors for cleaning and washing agents, and additives (UC = 9), are 0 to air and 1 (100 per cent) to wastewater.

Therefore, based on this information, the emission is expected to be exclusively to wastewater. However, D4 is highly volatile and so this assumption may not be correct. To take this into account, for the preliminary calculation the split between emissions to air and to wastewater is assumed to be 0.25 (25 per cent) to air and 0.75 (75 per cent) to wastewater.

Further information on the actual emission pattern would be useful to refine these estimates.

3.1.5 Other or unspecified uses

According to the figures given in Section 2.3 a very small amount of D4 is currently unaccounted for (given as other or unspecified uses). It is not clear if these small tonnages represent actual new uses that are not already covered in the assessment or result merely from the different ways companies report their data. However, as the tonnages involved are generally small, they are not considered further in this assessment.

3.1.6 Other sources of emission

3.1.6.1 Impurities in PDMS polymers

PDMS-based polymers may contain residual amounts of D4, which may subsequently be lost via volatilisation during the lifetime of these polymers. CES provided figures for the amounts of residual monomer in PDMS-based products and these are summarised in Table 3.1 (EU) and Table 3.2 (UK).

Table 3.1 D4 impurities contained in silicone products (total EU)

Application	2004 EU sales (tonnes)	Residual monomer content (%)	Amounts of residual monomer (tonnes)
Sealants	210,000	0.043	90.9
Elastomers	139,000	0.195	271.4
Fluids and specialities	204,000	0.336	686.1
Silanes	60,000	0	0
Resins	20,000	0	0
Total	633,000		1048.4

Table 3.2 D4 impurities contained in silicone products (UK)

Application	2004 UK sales (tonnes)[1]	Residual monomer content (%)	Amounts of residual monomer (tonnes)
Sealants		0.043	13.1
Elastomers		0.195	41.9
Fluids and specialities		0.336	101.1

Silanes	0	0
Resins	0	0
Total		156.2

Note: [1]Full figures are not available. Where data are missing they are estimated from total EU sales assuming that the UK accounts for 15 per cent of the total sales.

With the exception of elastomers, the figures relate to the amount of the monomer in the PDMS polymers as sold. For elastomers the figures refer to the amount of monomer released to air during the post-curing of silicone rubbers.

Toub (2002) considered the factors that affect the levels of volatile products present in fabricated silicone elastomers. The total level of volatile silicone products (including both linear and cyclic siloxanes) varies according to the particular formulation, manufacturing process, shape of the manufactured article, and storage conditions, but is generally in the range 0.05–3 per cent by weight in the cured silicone rubber product. Example contents of various cured high-consistency rubber sheet products are in the range <0.01–0.61 per cent by weight for D4, <0.01–0.42 per cent by weight for D5, and <0.01–0.37 per cent by weight for D6. The level depends on the actual rubber formulation and the thickness of the article. The sheet exposure time was an important factor in relation to the residual levels. For example, after storage for one week the residual level of D4 in the cured rubber is below the detection limit, independent of the thickness of the article. Post-curing for two hours at 200°C also reduced significantly the residual amounts of D4 present in the product.

As a first approximation it is assumed that all of the residual monomer is lost from the PDMS product by volatilisation during the first year of use. On this basis the UK, regional (taken as 10 per cent of the total EU), and total EU emissions of D4 from this source are estimated as:

- total UK, 156,200 kg/year to air
- Regional, 104,840 kg/year to air
- total EU, 1,048,400 kg/year to air.

3.1.6.2 Breakdown of PDMS polymers

A number of literature sources indicate that D4 (and other cyclic oligomeric siloxanes) can form during the breakdown of PDMS. In this Section we focus on the most relevant studies to investigate this breakdown process, rather than provide an in-depth review of the overall degradation of PDMS and other silicone polymers (this is beyond the scope of the current risk assessment).

In many of these studies the PDMS used is specified in terms of the viscosity, as this is usually used to classify the various types of PDMS fluids (Chandra, 1997):

- low viscosity, kinematic viscosity in the range 0.65–20 centistokes (cst)
- medium viscosity, kinematic viscosity in the range 50–1000 cst
- high viscosity, kinematic viscosity in the range 5000 to 250,000 cst
- gums, kinematic viscosity >500,000 cst.

The relevant information on the identity of the substance (i.e. viscosity and other data) is given for each study wherever available.

Weschler (1988) showed that five main cyclic siloxanes are formed when samples of PDMS (viscosities between 20 and 30,000 cst) are pyrolysed at temperatures of between 700 and 980°C for one second (the atmosphere used in this study is not totally clear, but appears to have been helium). The relative abundances of the products formed are relatively constant over the range of PDMS products studied, with the products D3, D4, D5, D6, and tetradecamethylcycloheptasiloxane (D7) in the approximate ratio of 100:36:13:8:6, respectively. No information is given on the yields of volatile products that form under these conditions. The author notes that this product distribution was similar to that in earlier work by Thomas and Kendrick (1969) in experiments using a vacuum at 420°C for five hours.

Grassie and Beattie (1984) report that PDMS (no information is given on the identity) starts to emit volatile products (as shown by thermal volatilisation analysis) at 343°C, and this reaches a maximum rate at 443°C. The volatile products that formed are mainly D3, with smaller amounts of D4. The yield of these products is not given. The incorporation of aromatic structures into the polymer chain backbone increases both the threshold temperature for the degradation and the temperature at which the maximum rate of volatile emissions occur.

Camino *et al.* (2002) report that earlier work shows that the thermal degradation of PDMS end-blocked with $(CH_3)Si–$ groups in inert atmospheres (e.g. N_2) and under vacuum results in depolymerisation and the formation of cyclic oligomers. The most abundant cyclic oligomer is D3, but irregularly decreasing amounts of D4, D5, D6, and higher oligomers can also form. In air the decomposition is accompanied by the formation of some silica powder. It is also reported that cationic reactions on glass surfaces can contribute to the thermal degradation of PDMS polymers.

Camino *et al.* (2002) carried out further experiments to investigate the mechanism of thermal degradation of PDMS [end-blocked with $(CH_3)Si–$ groups and containing a vinylmethylsiloxane unit every 1400th $–(CH_3)_2–Si–O–$ unit, with a viscosity of 8×10^6 mPa[9]). Experiments were carried out in either a helium or air atmosphere in a glass container, and two types of heating regime were used. The first involved a programmed temperature increase of 10°C/minute up to 80°C, equilibration for one minute, then a 10°C/minute increase from 80°C to 400°C, and finally held at this temperature for one hour. The second involved flash pyrolysis in which the sample was heated rapidly at 80°C/minute up to 800°C and then held at this temperature for ten minutes. The products evolved during the heating were collected and analysed. The programmed temperature-increase experiments show that the relative amounts of cyclic degradation products formed are 100:74:25:43:16 for D3, D4, D5, D6, and D7, respectively, under a helium atmosphere, and 100:67:32:44:18 for the same products under an air atmosphere. Higher cyclic siloxane oligomers also form in smaller amounts. The actual absolute yields of the products are not given, but it is indicated in the paper that the major volatile products from the experiments in air are water and CO_2 (and also silica), which result from the gas-phase oxidation of the volatile cyclic oligomers formed.

The flash pyrolysis experiments show that linear siloxane oligomers and rearranged siloxane compounds are formed, along with the cyclic siloxane oligomers. Under these conditions D4 is the dominant cyclic oligomer (with a relative abundance of 85:100:37:27:17 in a helium atmosphere and 56:100:31:23:18 in an air atmosphere for the products D3, D4, D5, D6, and D7, respectively). Oxidation of the volatile products into CO_2, water, and silica is more limited under these conditions in the air atmosphere than in the slow-heating experiments. Again, no information is given on the absolute yields of volatile products that form under these conditions.

[9]The viscosity is given in the paper as mPa, but this unit is not normally associated with viscosity. It may be that the actual unit should be millipoise (mP) or mPa s (both are units of dynamic viscosity 1 mPa s = 10 mP). To convert from dynamic viscosity into kinematic viscosity, the specific gravity of the fluid is needed (i.e. 1 cst = 1 centipoise/specific gravity).

Overall, Camino *et al.* (2002) conclude that thermal degradation of PDMS occurs through two competing mechanisms. The first is a molecular mechanism that forms cyclic oligomers. This involves scission of the Si–O bond and the reaction is favoured in flexible chains at lower temperatures. The second mechanism, which prevails at higher temperatures, is a radical one that involves homolytic scission of the $Si–CH_3$ bond. Cross-links then form within the molecule, which in turn decrease the flexibility of the PDMS and hinder the splitting of the cyclic oligomers.

Lomakin *et al*. (2003) also found similar products in thermal degradation studies by. In these experiments, samples of PDMS (molecular weight 10^7 g/mol with terminal methyl groups; the viscosity was not given) were pyrolysed at temperatures between 300 and 800°C in glass cells with flowing air. Under these conditions D4 is the dominant cyclic siloxane oligomer formed and accounts for 70.4 per cent at 300°C, 45.0 per cent at 400°C, 33.1 per cent at 500°C, 55.2 per cent at 600°C, 48.1 per cent at 700°C, and 39.0 per cent at 800°C of the total volatile products. D4 was also forms in similar experiments using a blend of polystyrene and PDMS (80:20 ratio). The actual yields of volatile products at the different temperatures are not listed in the paper. The results of thermogravimetric analysis are given graphically and generally show little weight loss from the PDMS polymer alone in air at temperatures up to around 300°C, with around 50 per cent weight loss by 500°C (no further weight loss appears to occur at higher temperatures).

Nielsen (1979) reports that significant degradation of PDMS occurs above 350°C in the absence of air and catalysts. Experiments carried out at 370°C with different PDMS products (PDMS fluids with viscosities of 50, 100, 1000 or 10,000 cst) under a nitrogen atmosphere form both cyclic and linear volatile polysiloxanes (including D4). The actual yields of volatile products at the different temperatures are not listed in the paper. The results of thermogravimetric analysis are given graphically and generally show little weight loss from the PDMS polymer alone in air at temperatures up to around 300°C, with around 50 per cent weight loss by 500°C (no further weight loss appears to occur at higher temperatures). The composition of the volatile products depends on the composition of the PDMS, and also changes with time as the composition of the residual PDMS fluid changes. For example, the 10,000 cst PDMS product gives only cyclic volatiles until much of the fluid is volatilised, whereas the 50–1000 cst PDMS substances evolve significant amounts of linear volatile products throughout the degradation.

Patel and Skinner (2001, 2003) found that cyclic polymethylsiloxane species, from D4 to D18, could be extracted from samples of room-temperature vulcanised polysiloxane rubbers (prepared by adding tin octoate catalyst to RTV5370 gum) thermally aged in inert gas atmospheres (argon), sometimes in the presence of moisture, at temperatures up to 190°C for 48 hours [longer term experiments were also carried out at lower temperatures (e.g. 80°C for six months) but few details of the results of these experiments are given]. The extraction was carried out by immersing the polymer in toluene at 70°C for 96 hours. Under these conditions (aging at 190°C for 48 hours) the amount of extractable matter is around 5.5 per cent of the initial weight of the polymer when the polymer is aged at 190°C in sealed containers and about 2.7 per cent of the initial weight when it is aged at 190°C in the open air (for comparison the amount of extractable matter from the virgin sample is 3 per cent of the initial weight of the polymer). The cyclic siloxanes contribute around 50 per cent of the weight of the extractable material from the aged samples (the contribution to the extractable material from the virgin sample is not clear). These substances are thought to form as a result of thermally activated degradation processes that involve depolymerisation reactions of the polymer chains. However, in practice room-temperature vulcanised rubber is not designed for use at high temperatures for extended periods of time. The emissions to air during post-curing of elastomers are considered in Section 0.

Although the results of the thermal degradation studies show that D4 forms under certain high-temperature conditions, under the usual conditions of use PDMS polymers are known to possess a high degree of thermal stability. According to CES (2005b) PDMS polymers are not recommended for use at temperatures greater than 150°C in contact with air. The silicone industry's guidance is also that under sealed conditions (exclusion of air) the average use-temperature should not exceed 250°C and the maximum temperature should not exceed 300°C. Also, most of the available pyrolysis studies were carried out at 300°C or higher and only limited information is available on the potential breakdown products formed at lower temperatures. (However, it is expected that PDMS and other silicone polymers become increasingly stable at lower temperatures. For example, although the above data show that D4 appears to make up a similar fraction of the total volatile products that form at each temperature, the amount of total volatile products formed varies with temperature and is likely to decrease with decreasing temperature below 300°C.) Overall, this means that the actual thermal breakdown of PDMS polymers during normal use is minimal, although it cannot be ruled out that D4 may form in some situations. It is not possible to quantify this potential source of D4 to air.

As well as thermal breakdown, PDMS polymers can also undergo degradation in soils. The products of this degradation depend, to a large extent, on the conditions used. Similar to the case with cyclic siloxanes (see Section 3.2.3) the degradation is an abiotic process related to the acid sites on minerals present in the soil and is sensitive to the water content of the soil. The relevant information on this for PDMS is summarised here.

Carpenter *et al*. (1995) studied the degradation of PDMS using a USEPA standard soil. The substance tested was ^{14}C-PDMS with a viscosity of 350 cst. The soil used had a moisture content of 2 per cent and was a sieved blend that consisted of 20 per cent soil, 20 per cent sand, 25 per cent silt, 5 per cent gravel, 22.5 per cent kaolinite, and 7.5 per cent montmorillonite. In the three spiking methods the soil was slurried with:

- a solution of PDMS in hexane and the hexane was evaporated under a stream of dry nitrogen;
- a solution of PDMS in hexane followed by filtration; an aqueous emulsion of PDMS, filtered and air dried to a 2 per cent moisture content.

The initial concentration was around 350–400 mg/kg. The spiked soils were then incubated (the temperature is not given) in covered glass jars. Degradation of PDMS was apparent in all systems after just a few hours (as seen by a change in the molecular weight distribution of the components of the polymer). Over longer periods (six months to one year) significant amounts of low molecular weight siloxanols formed. In the aqueous extract of the soil after one year of incubation, dimethylsilanediol was the major water-soluble degradation product, with smaller amounts of the dimer and trimer diols also present.

Carpenter *et al*. (1995) also carried out an experiment to investigate the formation of volatile products during the degradation. In this experiment the spiked soil was incubated for one week in a vessel swept with nitrogen. Volatile degradation products were collected using a charcoal trap. No cyclic siloxanes formed under these conditions. The principal products in extracts from the soil were a series of linear silanol-terminated oligomers with seven siloxane units or less.

The mass balance reported in this study is relatively low for soils incubated for long periods. This indicates that some of the low molecular weight breakdown products may be tightly bound to soil, consistent with the findings of Lehmann *et al.* (1994, 1995), Lehmann and Miller (1996), Xu (1998), and Xu *et al.* (1998). These show that as the soil dries binding of dimethylsilanediol to soil increases (i.e. the dimethylsilanediol is no longer easily extracted

with organic solvents, such as tetrahydrofuran, but is readily extracted by dilute aqueous acid solution).

Lehmann *et al.* (1994) showed that ^{14}C-PDMS (200 cst viscosity, number average molecular weight 6642 g/mol) degraded slowly when incubated in a Londo sandy clay loam soil with a water content of 12 per cent. The radiolabel in the substance tested was randomly distributed on the methyl groups. The soil was collected from an agricultural field in Michigan (top 5 cm), sieved (2 mm), and stored at 4°C prior to use. It had an organic matter content of 2.4 per cent, a pH of 7, and a sand:silt:clay ratio of 50:28:22.

The test system used consisted of 50 g of soil in biometer flasks to which 0.5 ml of a solution of PDMS in tetrahydrofuran was added to give an initial PDMS concentration of 100 mg/kg. The soil was left uncovered for three hours to allow the solvent to evaporate, and then CO_2 and volatiles traps were added. Next, the flasks were attached to an oxygen manifold and incubated at a constant moisture content at 25°C for up to 25 weeks. A second set of experiments investigated the effect of soil drying on the degradation rate. These samples were prepared in a similar way, except that 5 g of soil in centrifuge tubes was used, a foam plug moistened with PDMS (350 cst viscosity) inserted into the neck of the tube (to trap volatiles), and the tubes set open to dry at 25°C for up to 14 days.

In the experiments using moist soil (12.2–13.2 per cent moisture) the amount of water-extractable 14C in the soil increased with time, which suggests that the polymer degraded to smaller, water-soluble compounds. After 25 weeks of incubation the yield of low molecular weight water-soluble products was around 2.9 per cent of the radioactivity initially applied. The soil-extractable degradation products were low molecular weight linear siloxanols of general formula HO–[Si(CH3)2O]n–H.

A small number of volatile ^{14}C compounds were also evident (collected in the trap). These compounds were not identified, but accounted for around only 0.5 per cent of the applied radioactivity after 25 weeks. In addition, a small amount of $^{14}CO_2$ was found (around 0.19 per cent of the total ^{14}C applied). The overall mass balance from these experiments is generally very good (in the range 92.8–107.2 per cent), which indicates that all major degradation products are accounted for. When the soil was allowed to dry (from a moisture content of 12 per cent to around 3 per cent over the period of a week), degradation was much more rapid.

For the soil-drying experiments, the soil dried steadily from an initial water content of around 12 per cent to a water content of about 2–3 per cent by day four. After this time the water content remained relatively constant throughout the experiment. No degradation of PDMS was evident over the first three days of the experiment. On day four a decrease in the molecular weight distribution and a slight formation of water-soluble degradation products was evident. However, by day seven a significant breakdown of the PDMS to low molecular weight products had occurred and by day 14 the water-extractable and acid-extractable (0.1 M HCl) products accounted for around 18.2 and 11.5 per cent, respectively, of the total radioactivity applied. No significant amounts of volatile products formed (<0.11 per cent of the amount of radioactivity applied). The mass balance from this experiment s again very good (99.0–107.4 per cent).

Additional experiments on the microbial degradation of the low molecular weight products showed that dimethylsilanediol is the major ultimate degradation product.

Lehmann *et al.* (1994) conclude that the degradation of PDMS is probably not biological in origin, as it is more rapid at lower soil moisture contents, conditions that are less favourable to microbial populations.

A follow-on study that used seven soils from the USA of differing pH, percentage organic matter, texture, mineralogy, and geographic origin demonstrates the general applicability of

this degradation route (Lehmann *et al.*, 1995). Moist soils (initial moisture between 8 and 31 per cent, depending on the soil) were amended with ^{14}C-PDMS (viscosity 350 cst and number average molecular weight 9440 g/mol) and maintained at 23°C for up to 14 days (during which the soils were allowed to dry naturally). In all soils, PDMS degraded to low molecular weight, water-soluble products over the 14 days of the experiment (for one soil the experiment was extended to 28 days). The main degradation product is dimethylsilanediol. Other small silanols or cyclic siloxanes were either not detected or formed in only trace amounts. Additional experiments were carried out to investigate the effects of the loading rate on the degradation products seen with one soil (Londo soil). At loadings of around 100 mg/kg, the dominant degradation product is dimethylsilanediol, using both moist and oven-dried soil. However, at very high PDMS loadings (1 per cent or 10,000 mg/kg), a higher proportion of cyclic products (i.e. D4) formed. Taking these results, along with the earlier findings of Buch and Ingebrigtson (1979), it is concluded that the cyclic products formed are significant only at very high PDMS loadings, especially if they are rapidly volatilised from the soil by a stream of air.

Another study by Lehmann *et al.* (2000) investigated the degradation of a commercially available PDMS (viscosity of 350 cst) emulsion in field soils under natural conditions. Aqueous emulsions of PDMS were sprayed onto four soil plots (each 2.44 m by 2.44 m) in Michigan in May 1997 to give concentrations of 0 mg/kg (control), 215 mg/kg (low treatment), 430 mg/kg (medium treatment), and 860 mg/kg (high treatment). Soil cores (0–5 and 5–10 cm) were collected every two weeks over the following summer and analysed for total soil PDMS and decreases in molecular weight of the PDMS that remained. The concentration of PDMS decreased by 50 per cent within 4.5, 5.3, and 9.6 weeks for the low, medium, and high treatments, respectively. Dimethylsilanediol was the main degradation product identified in the soil columns (found in most samples at <5 per cent of the original PDMS concentration). A further application of the medium treatment level was carried out in late August. This showed a slow degradation of PDMS during the cool, wet, autumn months followed by around 40 per cent degradation over the winter months, with further, extensive degradation in the summer of 1998. These findings are consistent with the results of the laboratory studies, but substances that volatilised from the soil were not collected in this study.

Stevens (1998) published a summary paper of the degradative behaviour of PDMS in soils. This paper concludes that dimethylsilanediol is likely to be the major ultimate degradation product from PDMS in the environment. Dimethylsilanediol is very soluble in water (245 g per 100 g) and slowly biodegrades into $^{14}CO_2$ and silicic acid [$Si(OH)_4$], which provides a route for the ultimate mineralisation of PDMS.

Stevens (1998) also reports work by Carpenter (1996) that shows relatively slow degradation of ^{14}C-PDMS (viscosity 350 cst) in freshwater sediments. After one year around 5–10 per cent of the PDMS had degraded to dimethylsilanediol, and approximately 0.25 per cent of the applied radioactivity was found as $^{14}CO_2$.

Xu *et al*. (1998) showed that a range of different clay minerals (including kaolinite, montmorillonite, nontronite, beidellite, illite, chlorite, allophone, gibbsite, and goethite) commonly found in soils all catalyse the degradation of ^{14}C-PDMS (viscosity 350 cst) when exposed at a relative humidity of 32 per cent. The more effective minerals are those with higher proportions of Al–OH functional groups on the surface, and the rate of degradation is also related to the specific surface area of the mineral.

Xu (1998) investigated further the effect of moisture levels and exchangeable cation on the degradation of PDMS fluids by clay minerals. ^{14}C-PDMS was tested, but no information on the viscosity is given (by comparison with other studies carried out by this author it is likely that the substance was of low viscosity, probably around 350 cst). The minerals used included kaolinite, talc, and Arizona montmorillonite saturated with Na^+, Ca^{2+}, or Al^{3+}. In the

tests, freeze-dried clay mineral was weighed into 35 ml glass tubes (0.1 g mineral per tube), placed in desiccators at either 32 per cent or 100 per cent relative humidity), and equilibrated for five days at 22°C. Around 100 µl of ^{14}C-PDMS solution was then added to the tube and the tubes were flushed with air at the correct relative humidity for 15 minutes, sealed, and then replaced in the desiccator for up to 30 days. The initial PDMS concentration was ~2 g/kg. At various times during the study, tubes were sequentially extracted (the headspace was not analysed directly) and analysed for degradation products. A shift in the molecular weight distribution of the polymers indicates that degradation to lower molecular weight products occurs.

The main final degradation product found in this study was dimethylsilanediol, although some volatile cyclic products were evident in the experiments with Al-saturated montmorillonite at high humidity. This latter finding was based on the low mass balance of total ^{14}C from this clay and subsequent direct measurement of volatile products

[identified as D4 (major product), D3, and D5] in a follow-up study (the mass balance obtained for the other clays was close to 100 per cent, which indicates little or no volatile products form).

Degradation (hydrolysis) occurred predominantly through random scission of the Si–O–Si backbone of the polymer (the degradation pathway is similar for all clay types, exchangeable cations, and humidities studied). The degradation proceeded in two stages (both zero order on the PDMS concentration; these kinetics may be a consequence of the very high PDMS loading used). The rate of the first stage increases with the increase in polarising power of the exchangeable cation (i.e. Al^{3+} >>Ca^{2+}>Na^{+}) and decreased humidity.

Xu (1998) concludes that reaction proceeds via the hydrolysis of the PDMS to form linear silanols with three to five $Si(CH_3)_2O$ units. These intermediate products could degrade further to form dimethylsilanediol or could cyclise to form D4, D3, D5, etc. The actual products formed under any given conditions are thought result from the relative rates at which the linear silanols form from PDMS and these two competing reactions. Conditions that best favour formation of volatile cyclic products are a combination of high soil moisture and a rapid PDMS degradation rate. However, this combination is unlikely to exist in reality as the PDMS degradation rate decreases with increasing soil moisture content. Therefore the potential for volatile cyclic products to form from PDMS in soils under field conditions is considered to be low.

Similarly, Xu (1999) reports that cyclic siloxane oligomers could form in soils as a result of rearrangement and/or hydrolysis reactions (ring-chain equilibrium) of PDMS polymers. The cyclic products formed can be lost from the soil by volatilisation, or can themselves undergo degradation (see Section 3.2.3) and so the ultimate degradation product of PDMS in soil is again likely to be dimethylsilanediol. The hydrolysis is thought to be catalysed by soil clays, with clay minerals of low pH, such as kaolinite and montmorillonite, the most effective.

Traina *et al*. (2002) also investigated the degradation of PDMS in soil (a silt loam) under field conditions using test plots (5 m by 5 m) amended with anaerobically digested municipal biosolids. The study was carried out over a four year period after a single application of 0, 15, or 100 tonne/ha of municipal biosolids (which contained around 1272 mg/kg PDMS; the types of PDMS in the biosolids are not given). The plots were used to grow corn and soy bean during the test and were tilled to a depth of 10 cm each spring. The soil water level was >100 g/kg (10 per cent) over most of the test period. The half-life of PDMS was in the region of 876–1443 days in the top 10 cm of the plot under these conditions. When amended soils were brought into laboratory conditions and allowed to dry [the water content fell to <50 g/kg (<5 per cent) within two weeks], much more rapid degradation occurred (>80 per cent of the

PDMS was transformed into low molecular weight products within 20 days). This study did not investigate the formation of volatile degradation products.

In addition to these studies, Buch and Ingebrigtson (1979) demonstrated that high concentrations of PDMS[10] (~6000 mg/kg soil) were degraded in soil to form low molecular weight cyclic (including D4) and linear oligomers, and hydroxyl functional products (further details are given in Section 3.2.3). This study was conducted with a constant flush of air over the soil that could have affected the equilibrium between soil and air, and thereby promote the release of cyclic siloxanes from the soil. Therefore, although this study demonstrated the possibility that degradation of PDMS could form D4, it is not possible to extrapolate these results to the situation in the real soils.

In summary, PDMS-based polymers appear to be able to break down to form D4, D5, and D6 under certain conditions. This occurs in the laboratory when PDMS is heated to relatively high temperatures and also in soil at ambient temperatures at high loading rates (>2000 mg/kg). The emission to the environment that results from such processes is very difficult, if not impossible, to estimate as the yield of such products depends on the specific conditions to which the polymers are exposed.

In terms of a possible source of emission to the environment, the degradation of PDMS polymers in soil is probably the more important to consider. Thermal degradation requires exposure to high temperatures for extended periods and, although this could theoretically occur in some uses, the fraction of the total PDMS polymers produced that would be exposed to such conditions is likely to be small. Also, the extent of degradation is likely to be minimal because of the generally high thermal stability of the PDMS polymers. (The emissions of residual levels of D4, D5, and D6 in PDMS polymers under normal conditions of use are considered in Section 0.) For soil, a significant amount of PDMS is used in 'down the drain' products, such as personal care products, etc. The properties of PDMS polymers are such that removal during wastewater treatment is likely to be mainly by adsorption onto sewage sludge, which when spread onto soil is likely to provide a significant route of exposure. For example, Fendinger *et al*. (1997) measured PDMS levels of 290–5155 mg/kg in sewage sludge from eight WWTPs in North America, and found <0.41–10.4 mg/kg PDMS in soils from locations where sludge was applied. However, these conditions represent excessive loadings that would not normally be found under field conditions, even where the rates of sewage sludge application are very high (CES, 2005b). The available information indicates that, although cyclic siloxanes can be formed from degradation of PDMS under some situations, they are generally not the major products under field conditions.

A reliable quantification of the amounts of cyclic siloxanes that may be formed from PDMS degradation in soil and from incineration of PDMS requires an in-depth assessment of the use pattern, sources, and fate of PDMS in the environment. This is beyond the scope of this risk assessment. However, an attempt is made below to provide initial estimates of the possible magnitude of these emissions, but these estimates are highly uncertain, as a large number of assumptions and simplifications are made.

The approach is based on data presented in Chandra (1997). This report contains the results of a survey carried out in 1993 by the manufacturers of silicone products in the USA. The survey provides estimates of the amounts of silicone products emitted to wastewater or disposed of as waste to landfill or incineration over the life cycle of the product. The survey includes possible emissions from both use and disposal of the substances, but excludes

[10]A range of PDMS liquids were used in this study, including products with viscosities of 10, 50, 1000, 10,000, and 100,000 cst, and a ^{14}C-labelled product (viscosity not clear). It is not always clear from the paper which substance was used in which part of the test, but the experiments to indentify the volatile products appear to have used the ^{14}C-labelled substance and unlabelled substance with a viscosity of 50 cst.

emissions from use of the substances as site-limited intermediates for the production of other substances. The results of the survey are summarised in

Table 3.3.

Substance or application	1993 consumption (tonnes/year)[1]	Emission (tonnes/year)			Estimated emission factor (fraction of total consumption)		
		Wastewater	Landfill and/or incineration	Other and/ or soil	Wastewater	Landfill and/ or incineration	Other and/or soil
PDMS	138,000	13,590	24,810	13,380	0.0985	0.180	0.0970
Modified PDMS	15,300	742	3330	294	0.0485	0.218	0.0192
PEMS[2]	18,240	2690	7210	340	0.148	0.395	0.0186
Resins	7230	0	2420	310	0	0.335	0.0429
Elastomers	89,210	0	89,130	0	0	0.999	0
Total	267,980	17,022	126,900	14,324			

Table 3.3 Estimated emissions of PDMS-based products in the USA in 1993 (taken from Chandra, 1997)

Notes: [1]The consumption figures include the amounts used as site-limited intermediates. Emissions from site-limited intermediate use are not considered in the emission figures.
[2]PEMS is polyethermethylsiloxane.

For PDMS, Chandra (1997) indicates that the primary uses, other than as site-limited intermediates, were in industrial applications (e.g. as antifoams, softeners, and wetting agents in textile manufacturing, and as transformer dielectric fluids and heat-transfer liquids) and in consumer applications (such as personal care, and as household- and automotive-care products, such as polishes). Chandra (1997) estimates that the main source of release to wastewater is from use in personal care products and various processing aids. At the end of the product life cycle it is estimated that around 24,810 tonnes/year of PDMS is landfilled, incinerated, or recycled (largely as textile or paper coatings, but also in the form of electrical and mechanical fluids). In addition, it is estimated that around 13,380 tonnes/year disperses to the environment from use in household products (such as polishes) and some industrial applications (such as lubricants and mould-release agents).

Several types of modified PDMS are considered in the Chandra (1997) survey. Uses other than as site-limited intermediates considered in the survey are summarised as:

- methyl(phenyl)siloxanes – high temperature oil baths, greases, diffusion pump fluids, and paint additives;
- methyl(hydrido)siloxanes – waterproofers for textiles and wall boards;
- methyl(alkyl)siloxanes – release agents for plastic and urethane parts, cutting oils, and paint additives;

- methyl(aminoalkyl)siloxanes – many applications, including textile, personal care products, household-care products, automotive-care products, and plastic modification.

The estimated emissions to wastewater are thought to come primarily from the use of methyl(aminoalkyl)- or methyl(alkyl)siloxanes. The main sources to landfill and incineration are thought to be from uses such as textile coatings, high-temperature oil baths, wall-board coatings, rubber compounds, and powder treatment.

The main uses, other than as site-limited intermediates, of polyethermethylsiloxanes thought to lead to emissions to wastewater are from textile and personal care products. The main source for landfill and incineration is from use in urethane foam. In additives a direct emission to soil of around 340 tonnes/year is estimated from use as an agricultural adjuvant.

The main uses of cured resins identified in the Chandra (1997) survey are as electrical varnishes, moulding compounds, components of decorative and high-temperature paints, abrasion-resistant coatings, laminating and adhesive materials, masonry water repellents, adhesive promoters, and components of silicone pressure-sensitive adhesives. Virtually all of the resin that enters the environment is thought to be disposed of by either landfill or incineration. However, it is also thought that some resins used as components of coatings and paints, for example, may be subject to weathering and wear over time and so may result in diffuse emission to the environment over time. It is estimated that this may amount to around 310 tonnes/year.

The main uses of RTV elastomers considered in the Chandra (1997) survey are as sealants, encapsulants, foams coatings, caulking, and mould making. Heat-cured rubber applications include tubing, hoses, wire and cable insulation, penetration seals, laminates, release coatings, foams, and other moulded and extruded articles. Gel applications include electrical encapsulants and wound-dressing patches. It is estimated that virtually all of the elastomers are either landfilled or incinerated at the end of their life cycle.

From the data presented in Chandra (1997) it is possible to estimate emission factors based on the total consumption in the USA in 1993 (

Table 3.3). These emission factors are been used to estimate the possible emissions in the EU, using the EU consumption data for PDMS-based products and the known consumption

Substance or application	**1993 consumption (tonnes/year) 1**	**Emission (tonnes/year)**			**Estimated emission factor (fraction of total consumption)**		
		Wastewater	Landfill and/or incineration	Other and/ or soil	Wastewater	Landfill and/ or incineration	Other and/or soil
PDMS	138,000	13,590	24,810	13,380	0.0985	0.180	0.0970
Modified PDMS	15,300	742	3330	294	0.0485	0.218	0.0192
PEMS2	18,240	2690	7210	340	0.148	0.395	0.0186
Resins	7230	0	2420	310	0	0.335	0.0429
Elastomers	89,210	0	89,130	0	0	0.999	0
Total	267,980	17,022	126,900	14,324			

rates for 2004. The emissions that result are summarised in Table 3.4. The assumptions made in these estimates are that the:

- overall use pattern for PDMS-based products in the USA in 1993 is also applicable to the EU in 2004;
- emission factor for PDMS derived from Chandra (1997) is applicable to the use of PDMS fluids in the EU [the main uses of PDMS considered in the Chandra (1997) survey leading to emissions to the environment were fluid uses];
- emission factor for elastomers from the Chandra (1997) survey is applicable to both elastomers and sealants.

The Chandra (1997) survey effectively provides a mass-balance approach for the ultimate fate of the total consumption in the USA in 1993. It is assumed here that the data can be used to estimate a yearly emission from the yearly consumption figure. However, the emissions identified in the Chandra (1997) survey do not necessarily occur within the same year. For example, disposal to landfill occurs at the end of the article's lifetime, which may be many years after the article was produced. Implicit in the assumption to estimate the yearly emissions from the yearly consumption figure is that for any emission for substances with long lifetimes, a 'steady-state' situation exists at some point in time assuming a constant consumption rate. For example, if a product has a lifetime of ten years and is then disposed to landfill, there is no disposal over the first nine years, but from the tenth year onwards the amount disposed corresponds to the amount produced in that year. A similar argument can be applied to substances and products that are continuously emitted during use and the product is used over more than one year.

Table 3.4 Estimated emissions of PDMS-based products in the EU

Application	2004 EU sales (tonnes/ year)	Assumed emission factor (fraction of total consumption)			Emission (tonnes/year)		
		Wastewater	Landfill and/or incineration	Other and/ or soil	Wastewater	Landfill and/or incineration	Other and/ or soil
Sealants	210,000	0	0.999	0		209,790	
Elastomers	139,000	0	0.999	0		138,861	
Fluids and specialities	204,000	0.0985	0.180	0.0970	20,094	36,720	19,788
Silanes[1]	60,000	N/A	N/A	N/A	N/A	N/A	N/A
Resins	20,000	0	0.335	0	0	6700	0
Total	633,000				20,094	392,071	19,788

Note: [1]Silanes are non-polymeric products used mainly as intermediates in the production of other products. They are not relevant to the discussions here.

The next stage is to estimate the amount of D4 that may be emitted to the environment from the PDMS-based products.

Some products have structural differences to PDMS and therefore it may not be possible to estimate the amount of D4 emitted from them using the available data for PDMS. For example, the polyethermethylsiloxanes generally have a high polyether content (30–80 per cent) and so the environmental fate of these products may be different than that of for PDMS (Chandra, 1997). The amounts of polyethermethylsiloxanes used in the EU are not given separately in the consumption figures (they are probably included in the fluids and specialities uses).

In particular, it is not clear whether the degradation of resins and elastomers in the environment is similar to that of PDMS. Both resins and elastomers are cross-linked, intractable solids. Chandra (1997) reported that silicone elastomers do not appear to be degraded in landfills, possibly as a result of their limited bioavailability in the environment. Therefore biodegradation of both resins and elastomers is not considered to be a source of D4 in the environment. The same considerations could also apply to sealants, which again have a degree of cross-linking in their cured state.

Therefore, in terms of the potential to form D4 from biodegradation, emissions of PDMS fluids and specialities are likely to be the dominant source. As shown in Table 3.4, for the EU it is estimated that around 20,100 tonnes/year are emitted to wastewater, 36,800 tonnes/year are disposed of via landfill and incineration, and 19,800 tonnes/year are released from diffuse sources in the EU, probably mainly to soil.

To provide a rough estimate of the amount of cyclic siloxanes that could be emitted from this source, the assumptions made are:

- The amount of cyclic siloxanes and other volatile product emitted during the degradation in soil is around 0.5 per cent of the PDMS added to the soil (based on Lehmann et al., 1994).
- The typical WWTP connection rate in the EU is 80 per cent (the default value from the TGD) and the majority of PDMS fluids that enter a WWTP adsorb onto the sludge and are subsequently applied to agricultural land. This then amounts to ~16,080 tonnes of PDMS fluids.
- Of the amount disposed of, it is assumed that 72 per cent is landfilled, and 7 per cent incinerated (with the remainder treated by other methods). This is based on the known pattern of waste treatment in England and Wales in 2004–2005 at waste-management facilities licensed or permitted by the Environment Agency.11 Thus the estimated amount of PDMS fluids landfilled in the EU is ~26,500 tonnes/year, with ~2600 tonnes/year incinerated.
- The amount of D4 formed during the degradation is assumed to be around 25 per cent of the total cyclic siloxanes and other volatile products. The actual identity of the volatile products formed in the Lehmann et al. (1994) study was not determined. This is a significant source of uncertainty in the estimates.

The amount of PDMS fluids thought to reach soil (either from diffuse emissions or the application of sewage sludge) is therefore estimated as ~35,900 tonnes/year. Assuming that 0.5 per cent of this degrades into cyclic siloxanes and other volatile products, the total amount of such products formed is estimated as around 179,500 kg/year. Thus the amount of this that could be D4 is estimated as around 44,875 kg/year. This represents a volatile loss from the soil and should be considered as an emission to air.

It is estimated that around 26,500 tonnes/year of PDMS fluids could be disposed of to landfills in the EU. The conditions in landfills are typically anaerobic in nature and little

[11] See http://www.environment-agency.gov.uk/subjects/waste/?version=1&lang=_e.

information is available on the degradation of PDMS under such conditions. If it is assumed again that the yield of cyclic siloxanes and other volatile products during degradation in landfills is around 0.5 per cent, with 25 per cent of this comprising D4, the amount of D4 emitted could be around 33,125 kg/year. However, this figure is highly speculative as the actual behaviour of PDMS under anaerobic conditions is unclear.

To determine the significance of this source in comparison to releases from the direct uses of D4, these estimated emissions of 44,875–78,000 kg/year should be compared with the total estimated EU emissions of D4 to air. The total EU emission to air is confidential, but the estimated emission from PDMS breakdown is <3 per cent of this. Therefore, although there are large uncertainties in the approach used here to estimate the emissions from degradation of PDMS polymers, this does not appear to be a major source of D4 in the environment when compared with the emissions from direct uses of D4, and so it is not considered further in the assessment.

It is not currently possible to estimate the amount of D4 that may be in the soil from the degradation of PDMS polymers. This is considered in relation to the PECs calculated for soil in Section 0.

It is also estimated that a substantial amount of other polymeric siloxane products (such as sealants, elastomers, and resins) may be emitted to the environment and, in particular, may be disposed of into landfill. It is assumed here that because these substances have a substantial amount of cross-linking in the polymer, they are less degradable than PDMS fluids and so their potential to emit cyclic siloxanes from degradation is much lower. However, little actual information appears to be available as to how cyclic siloxanes form from such products under conditions found in landfills. Therefore it is not possible to evaluate fully this potential source here. This is considered in Section 0.

As well as by landfill, PDMS liquids and other polymeric siloxane products are also disposed of by incineration. It is not possible to estimate the amounts of cyclic siloxane products formed during high-temperature incineration processes. As noted earlier, a number of available studies show that cyclic siloxanes may be formed under high-temperature pyrolysis conditions, but the relevance of these studies to the conditions of incineration (i.e. in the presence of flames) is uncertain.

However, it is thought that the conditions effectively destroy any cyclic products formed, and so the emissions of D4 from incineration are expected to be small compared with those from other sources of D4 emission. This is considered in Section 0.

3.1.6.3 Other sources

Some data reported in the literature suggest sources of D4 emission other than those considered elsewhere in this assessment. These data are summarised here. However, in general, information is scarce on the quality-control methods used in the analyses. While this in itself does not mean the data are unreliable, there are potential problems of contamination in the analysis of D4 (see Section 3.3 for more details). It is possible that some of the reported occurrences of D4 from these sources result from analytical artefacts and do not themselves represent significant sources of emission of D4 to the environment.

Jay and Stieglitz (1995) detected, but did not quantify, D4 in the flue gas from a municipal waste incineration plant (.

The emissions from waste-incineration processes are expected to be low, as small-scale pool-burning tests indicate that cyclic siloxanes with boiling points of around 250°C and lower (i.e. D4, D5, and D6) burn rapidly and completely (indeed, more rapidly than hydrocarbons of similar volatility) to form CO_2, water, and amorphous silica without ash formation (Lipowitz and Ziemelis, 1976; Stevens, 1996). Siloxane products with higher boiling points (such as PDMS fluids and polymers) burn less readily and must firstly undergo thermal rearrangement to form more volatile cyclic siloxanes (this process is slow at temperatures <350°C), which are then readily combusted. Therefore the emissions of D4 from waste incineration are likely to be low and so this potential source is not considered further here. Although D4 is reported in the flue gas from a municipal waste incinerator (see above), it is also possible that, because of the difficulties in analysing low concentrations of D4, this could be an analytical artefact rather than an actual emission in the flue gas.

Salthammer (1997) investigated, using 1 m^3 glass chambers, the emissions of VOCs from 44 samples of wood coated with various furniture coatings. The sample loading rate used was 1.0 m^2/m^3 and the experiments were carried out at 23°C, at a relative humidity of 45 per cent and using an air exchange rate of one per hour. D4 was found in the chamber air from three of the samples. No further details are given on the emission rates or concentrations found. As there is currently no reported use of D4 in coatings these data could reflect a historic use of D4, represent emissions from unreacted D4 in PDMS polymers (and so the emissions are already accounted for in Section 0), or most likely the D4 found was an analytical artefact (e.g. see Section 3.3).

In chamber experiments, Hillier *et al*. (2003) detected several oligomeric siloxanes (including D4) in the volatiles emitted from various samples of flexible foam mattresses. However, the same siloxanes are also emitted from various raw materials used to make the foams (e.g. polyols). This is thought to be an analytical artefact from the breakdown of the PDMS layer on the needles used for sampling and sample injection. The paper indicates that, as these needles were not used in the experiments with the foam samples themselves, it is unlikely that this source of contamination occurred. However, given the findings with the polyol experiments, the results from the flexible foam experiments must be considered uncertain. Therefore this is not considered to be a significant source of emission of D4 to the environment.

Rosati *et al.* (2007) found that D4 was released during the cooking of some types of microwave popcorn. The quality-control procedures used in this study included the analysis of blanks daily, and it appears that D4 was not detectable in these blanks.

The source of D4 in these experiments is unclear.

A number of occurrences of D4 emitted from landfill sites are reported. For example, D4 was found in biogas from four landfill sites in the USA (Niemann, 1997). The concentration present (as a combined total with D5) was in the range 1–5 mg/m^3. Similarly, Schweigkofler and Niessner (1999) found D4 in biogas samples from two landfill sites in Germany at a concentration of 4.2–8.8 mg/m^3. Also, Schwarzbauer *et al.* (2002) found D4 in landfill leachate at a sanitary landfill in Germany. The concentration is not given, but the detection limit of the analytical method used was around 50 ng/l. Thörneby *et al.* (2006) reported D4 in samples of landfill leachate from Sweden (the level found is not stated).

Similarly dos Santos Freitas *et al*. (2004) found D4 in a municipal waste landfill leachate sample from Brazil (the level was not determined). The source of D4 in the landfills studied is not clear, but could include disposal of products that contain D4 (such as personal care products, etc.) or that contain PDMS polymers with the subsequent emission of unreacted D4 (see Section 0) or the subsequent breakdown of the PDMS polymer to form D4 (see Section 0). It is not possible to quantify the actual amounts of D4 that may be emitted to air and to leachate from landfill sites in the UK and EU. However, these emissions are likely to be at least partly covered by the worst-case approach taken to estimate the regional and continental emissions elsewhere in this report.

Jann and Wilke (2006) report that D4 is emitted from some hardcopy devices, such as printers, copiers, and multifunctional devices. It is not clear if the emissions are related to use of D4 itself or to a D4 impurity in PDMS-based polymers used within the device. In addition, few details are given on the quality-control measures used in the analysis.

3.1.7 Summary of worst-case emission estimates

The preliminary worst case emission estimates for D4 are summarised in

Table 3.5. The continental emissions represent the total EU emissions minus the regional emissions. For the environmental modelling at the regional and continental level an 80 per cent connection rate to the WWTP is assumed.

Table 3.5 Summary of emission estimates for D4

Scenario	Local emission		Regional emission (kg/year)	Continental emission (kg/year)
	Amount (kg/day)	Number of days		
Production and on-site use as an intermediate –UK site	Confidential to air 0.078 to surface water	300	Confidential to air 23.4 to surface water	Not quantified
Chemical intermediate – off-site – polymers – wet process – UK site	1.6 to air 0.1 to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Chemical intermediate – off-site – polymers – wet process – EU site	10.8 to air 5.6×10^{-5} to wastewater			
Chemical intermediate – off-site – polymers – dry process – UK sites	10 to air 0 to waste water	13		
Chemical intermediate – off-site – polymers – dry process – EU sites	74 to air 0 to wastewater	300		
Chemical intermediate – off-site – silica – UK and EU sites	2 kg/day to air 0 to wastewater		Confidential to air 0 to wastewater	Confidential to air 0 to wastewater
Personal care products – formulation – UK sites	5.2×10^{-6} to 4.7×10^{-3} to air 4.3×10^{-5} to 0.021 to wastewater	300	10.5 to air 52.1 to wastewater	92.7 to air 459 to waste water
Personal care products – formulation – generic site (non-UK)	0.002 to air 0.009 to wastewater	300		
Personal care products – use	3.8×10^{-3} to wastewater	365	25,200 to air 2800 to wastewater	485,100 to air 53,900 to waste water
Household products – formulation	Confidential to air Confidential to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Household products – use	Confidential air Confidential to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Residual monomer in PDMS			104,840 to air	943,560 to air
Breakdown of PDMS			Not quantified	Not quantified
Total[1]			Confidential	Confidential

Note: [1]The totals take into account the 80 per cent connection rate to the WWTP.

A further emission of 44,875–78,000 kg/year of D4 to air is estimated from the possible degradation of PDMS polymers in soil and landfills in the EU. However, this is subject to a large uncertainty and so has not been taken into account in the total emissions estimated in

Table 3.5. As it is estimated that this source only makes a relatively small contribution to the total emissions to air, it is not thought to impact significantly on the PECs that result.

3.2 Environmental fate and distribution

Responses to the recommendations of the Interagency Testing Committee (ITC) under the US Toxic Substances Control Act (TSCA) generated much of the data available on the environmental fate and behaviour of D4 (Walker and Smock, 1995), and so has undergone a peer review process in the USA. Much of these data are now published in review articles in the open literature. The essential details of the tests are reported here because many of the tests were carried out using modified test systems to address the inherent problems of testing D4 (low water solubility, high volatility). It is therefore important to understand the precautions taken to ensure concentrations were maintained during the test when we select the most appropriate data for use in the risk assessment. These details are generally taken from the published reviews of the data; the original laboratory test reports have not always been re-evaluated as part of this work.

3.2.1 Atmospheric degradation

3.2.1.1 Photo-oxidation

Two experimentally determined values for the rate constant for reaction of D4 with atmospheric hydroxyl radicals (k_{OH}) are available. Both were determined using the relative rate method. Atkinson (1991) determined the value of k_{OH} as 1.01×10^{-12} cm^3/molecule/s at 24°C, and Sommerlade *et al.* (1993) determined k_{OH} as 1.26×10^{-12} cm^3/molecule/s, again at 24°C. There is good agreement between the two determinations. A further value (from an unpublished study) of k_{OH} of 3.08×10^{-12} cm^3/molecule/s^{-1} is given in IUCLID (2005), but no further details are given.

Sommerlade *et al.* (1993) identified the major products from the reaction of D4 with hydroxyl radicals as heptamethylhydroxycyclotetrasiloxane, along with smaller amounts of heptamethyl(hydroperoxymethyl)cyclotetrasiloxane and 1,2-bis(heptamethylcyclotetrasiloxanyl)ethane, and trace amounts of heptamethyl(hydroxymethyl)cyclotetrasiloxane and bis(heptamethylcyclotetrasiloxanyl)ether. The hydroxyl-substituted products are expected to be more soluble in water than D4, and to have a lower vapour pressure, and so are likely to be removed from the atmosphere by wet and dry deposition (Chandra, 1997). Chandramouli and Kamens (2001) confirmed this for a related substance (D5). In this study nonamethylhydroxycyclopentasiloxane was identified as the main degradation product from D5 using an outdoor smog chamber that contained fine road dust. More than 99 per cent of the hydroxy derivative formed partitioned onto the dust particles.

Atkinson (1991) also determined experimental values for the rate constants for reaction with atmospheric ozone and NO_3 as $<3 \times 10^{-20}$ cm^3/molecule/s and $<2 \times 10^{-16}$ cm^3/molecule/s, respectively. The values refer to a temperature of 24°C.

The rate constant for the reaction of D4 with atmospheric hydroxyl radicals is estimated as 1.20×10^{-12} cm^3/molecule/s using the AOP(v1.91) program that is part of the USEPA EPI (v3.12) estimation software.

Abe *et al*. (1981) investigated the photodegradation of D4 in ozone at 25°C. Experiments were carried out using either oxygen and helium (20:80) or oxygen and nitrogen (20:80) atmospheres with an initial ozone concentration of around 10^{-3} mol/l. Degradation half-lives for D4 of around 0.5–2 hours are obtained under these conditions. The degradation rate is very sensitive to the presence of water –the rate increases with the addition of small amounts of water. It is thought that this occurs because reactive hydroxyl radicals (or singlet oxygen species) form from the ozone in the test system in the presence of water.

The half-life of D4 decreased linearly with the increasing initial concentration of ozone over the range 5.5×10^{-5} M to 1.6×10^{-3} mol/l (indicates a first-order dependence of the reaction rate on the ozone concentration). The linear relationship is:

$$\log t_{½} = -1.21 \log [O_3]_0 - 1.75 \qquad (3.1)$$

where $[O_3]_0$ is the initial ozone concentration (in mole/l) and $t_{½}$ is the degradation half-life of D4 (in minutes).

Using Equation (3.1) to extrapolate to 'typical' concentrations of ozone in the environment [around 10^{-9} mol/l for urban locations (Abe *et al*., 1981)], a half-life of >2500 years is estimated for this reaction. There is a large uncertainty in this estimated value as it is extrapolated well beyond the range tested experimentally, but it does indicate that the direct reaction of D4 with ozone is likely to be much less important than the reaction with hydroxyl radicals.

Abe *et al*. (1981) found a large number of degradation products in the reaction mixture after irradiation for four hours, generally with molecular weights in the 300–623 g/mol range (. These compounds are thought to contain hydroxyl groups (by reaction with the hydroxyl radicals formed in the test system under the conditions used), which could in turn condense to form higher molecular weight siloxanes and water.

Whelan *et al.* (2004) assessed the atmospheric fate of VMSs and their degradation products. The assessment used a simple equilibrium-partitioning model to investigate the relative rates of removal of two representative VMSs (the linear decamethyltetrasiloxane and D4) and their siloxanol degradation products by reaction and atmospheric deposition. The modelling is based on the work of Atkinson (1991) and Sommerlade *et al.* (1993), which demonstrates that siloxanes break down in the atmosphere to form hydroxyl-substituted silanols by reaction with atmospheric hydroxyl radicals. As substitution proceeds the silanols become increasingly water-soluble and less volatile, and so tend to be washed out of the atmosphere by wet deposition. Silanols are also assumed to be subject to hydrolysis reactions when dissolved in liquid water droplets. Removal by dry deposition is also accounted for in the approach, but scavenging of particulates from the air by wet deposition is not. The findings indicate that the parent siloxanes and the monohydroxy degradation products occur mainly in the vapour phase, with relatively small amounts associated with the water and particulate phases (although the small size of the water- and particulate-phase compartments in the atmosphere means that the concentrations in these phases can approach or exceed those in the vapour phase). The degradation products of the hydroxyl substitution are thought to be associated mainly with the dissolved and particulate phases. However, the decreasing concentration of precursor molecules as this degradation proceeds means that the maximum dissolved- and particulate-phase concentrations occur for degradation products with two hydroxyl substituents. The concentrations of degradation products with higher levels of hydroxyl substitution are predicted to decrease markedly with increasing substitution. The siloxanediols in the precipitation are predicted to undergo further reaction via hydrolysis, to give a mixture of siloxane products (depending on the atmospheric residence time and the pH). Overall, it is concluded that >99 per cent of the VMSs are removed from the atmosphere as silanols in wet deposition and <1 per cent in dry deposition.

Assuming an average atmospheric hydroxyl radical concentration of 5×10^5 molecule/cm^3 and a rate constant of 1.01×10^{-12} to 1.26×10^{-12} cm^3/molecule/s, the atmospheric half-life for D4 is estimated as 12.7–15.8 days. A half-life of around 14 days (the approximate mean of the two estimates) is assumed in the assessment. Degradation by reaction with other atmospheric photo-oxidants is likely to be negligible compared with that by the hydroxyl radical reaction. The products from the reaction are expected to be silanols, which are removed from the atmosphere by wet deposition. Buch *et al.* (1984) demonstrated that dimethylsilanediol and other water-soluble dimethylsiloxanols can degrade further through aqueous photolytic oxidative demethylation reactions. The final products of the degradation of dimethylsiloxanols are expected to be silicic acid and/or silica and CO_2 (Buch *et al.*, 1984; Chandra, 1997).

3.2.1.2 Photolysis

Abe *et al*. (1981) found that D4 only degraded slowly in the gas phase when exposed to light of wavelengths >290 nm in the absence of photo-oxidants. Over two days, only around 2 per cent degradation occurs on exposure of D4 to light in a pure oxygen atmosphere at 25°C.

In contrast to this, IUCLID (2005) reports that results from unpublished studies appear to show that D4 is rapidly photolysed in the atmosphere. Summary details of the experiments are available and show a half-life for D4 of 0.31 days when exposed to light of wavelengths between 290 and 450 nm (maximum intensity at 370 nm). Demethylated silicon compounds and CO_2 were the main degradation products seen. However, IUCLID (2005) also gives the details of another similar (possibly the same) study that indicate that the experiments were carried out in the presence of nitric acid or nitroethane (to generate hydroxyl radicals) and so it is probable that the reaction is with hydroxyl radicals rather than direct photolysis.

Therefore degradation of D4 by direct photolysis is not likely to be a significant in the environment.

3.2.2 Aquatic degradation

3.2.2.1 Hydrolysis

Dow Corning (2004, 2005) determined the hydrolysis of D4 using the OECD 111 test guideline, modified to take account of the volatility of D4 (OECD, 2005).

The first study was a preliminary study (Dow Corning, 2004). ^{14}C-D4 was tested (the purity was not determined, but no impurities were noted on analysis of the time zero samples from the experiment). Stock solutions of this were prepared in tetrahydrofuran, aliquots (10 µl) of this stock solution added to 50 ml of buffer solution (either pH 5, 7, or 9), and the spiked solution transferred to a series of glass reaction tubes that were immediately heat sealed (the headspace in the tube was estimated as around 6 per cent of the total volume). The initial D4 concentration was around 28 µg/l. The tubes were then incubated at 25°C in the dark prior to analysis. The analysis consisted of total ^{14}C determinations and more specific analysis for parent compound and metabolites. The half-lives determined are 33 hours at pH 5, 69 hours at pH 7, and 0.6 hours at pH 9.

The second, definitive study was carried out at 10, 25, or 35°C at each of pH 4, 7, and 9 (Dow Corning, 2005). ^{14}C-D4 with a purity of 98.0 per cent was tested. The test solutions

were prepared using a similar method to the that of the preliminary study. The initial D4 concentration tested was around 20 µg/l, and the test solutions also contained a small amount (0.8 per cent vol/vol) of the tetrahydrofuran carrier solvent. The recovery of total ^{14}C was determined at time points in the study. This shows average recoveries of between 63 and 87 per cent in the various individual experiments, with an overall average of 78 per cent. Although the average recovery is below that recommended in the test guideline

(90–110 per cent), the variability of the recovery within any one experiment is generally low (≤15 per cent in most experiments up to a maximum of 20 per cent). In terms of the reliability of the derived kinetic data, the relative variability in the total ^{14}C recovered within any one experiment is much more important than the absolute recovery overall, and so the low overall recovery is unlikely to have significantly affected the results of the test (the low overall recovery most probably results from volatile loss of the substance during the preparation of the test solutions). The recovery experiments also demonstrate that little or no physical adsorption of the test substance or hydrolysis products onto the walls of the test chambers occurred during the test.

The first-order hydrolysis half-lives obtained from the study are summarised in Table 3.6.

Table 3.6 Hydrolysis half-lives determined for D4

pH	Half-life (hours)		
	10°C	25°C	35°C
4	4.8	1.8	0.89
7	54.2	69.3 [1] 91.4 [1] 144 [1]	24.9
9	6.4 [1] 5.6 [1]	0.90 [1] 1.0 [1]	0.19 [1] 0.22 [1]

Note: [1]Separate determinations.

Four main hydrolysis products and intermediates were found (but not identified) in both the preliminary and the definitive studies. The HPLC chromatographic behaviour, and the pattern of appearance and disappearance of these products, is consistent with a mechanism that involves initial hydrolysis of D4 to form the linear octamethyltetrasiloxane-α,ω-diol, followed by subsequent hydrolysis to form the smaller linear dimethylsiloxane-α,ω-diol oligomers. The final product from this process is dimethylsilanediol.

The results reported in Table 3.6 are based on the results from the earlier part of the decay curve obtained for D4 (Dow Corning, 2005). At longer time periods (after around 70 per cent of the D4 has degraded), the degradation curve appears to deviate from that expected for a first-order process. This is thought to result from a degree of reversibility in the initial step of the reaction (the formation of linear octamethyltetrasiloxane-α,ω-diol). Further, non-linear analysis of the kinetic data enables us to estimate the rate constant for the reverse reaction (the formation of D4 from octamethyltetrasiloxane-α,ω-diol) in a number of experiments. Under the experimental conditions used, it is concluded that the extent of reversibility is minor; the ratio of the first-order rate constant for hydrolysis of D4 compared with that for the reverse reaction is estimated as around 6.7 at pH 7 (and of a similar order at pH 9). The octamethyltetrasiloxane-α,ω-diol itself was clearly shown to undergo further hydrolysis, which also limits the overall reversibility of the reaction.

Although the apparent deviation from first-order kinetics at longer time periods in the Dow Corning (2005) study is interpreted by the authors to indicate possible reversibility, other explanations may also explain the kinetics. For example, although not given in the report, the headspace in the tubes used may have been around 6 per cent of the total volume. This is based on the reported headspace for a study carried out with D5 under very similar conditions [both the D4 and D5 experiments used glass tubes of 4.2 mm internal diameter and 200 mm in length that contained around 2.2 ml of test solution and were flame sealed after spiking with the test substance (Environment Agency, 2008a)]. The dimensionless Henry's law constant (i.e. K_{aw}) for D4 is 24 (see Section 0), which implies that if equilibrium is achieved around 61 per cent of the total chemical in the glass tube may have been in the headspace and so not subject to hydrolysis. The gas phase may therefore have provided a buffer that resupplied chemical to the water phase as the D4 was hydrolysed, which may also explain the degradation curve seen.

The second-order reaction rate constants for the acid- and base-catalysed reactions are determined from the data at pH 4 and 9. These rate constants allow the hydrolysis half-life at any given pH to be determined, and are:

- acid-catalysed, kH3O+ (l/mol/h–1)::
  - 1.56 × 103 at 10°C
  - 3.91 × 103 at 25°C
  - 8.02 × 103 at 35°C;
- base catalysed, kOH- (l/mol/h):
  - 1.12 × 104 at 10°C
  - 7.10 × 104 at 25°C
  - 3.36 × 105 at 35°C.

Analysis of the variation of the first-order reaction rate constant with temperature at pH 4, 7, and 9 enabled the activation energy (E_a) and the Arrhenius constant (A) to be determined for both the acid- and base-catalysed process:

- acid catalysed:
  - Ea = 47.4 kJ/mol
  - A = 8.44 × 107/h
- base catalysed:
  - Ea = 96.5 kJ/mol
  - A = 7.42 × 1016/h

Using these data, half-lives of 16.7 days are estimated at pH 7 and 12°C (the TGD default conditions for the freshwater environment) and 2.9 days at pH 8 and 9°C (the TGD default conditions for the marine water environment).

The effect of this reversibility (if real) on the actual hydrolysis half-life of D4 in the environment is difficult to predict as the reverse reaction (formation of D4 from octamethyltetrasiloxane-α,ω-diol) is dependent on the concentration of octamethyltetrasiloxane-α,ω-diol in the environment. This is dependent on its rate of formation from hydrolysis of D4, its own rate of hydrolysis, and its possible presence in the environment from other sources. The actual concentration of D4 is unknown. If the only

source is hydrolysis of D4 itself, then it is possible that as the hydrolysis reaction proceeds according to the half-lives estimated above, a small, steady-state concentration of octamethyltetrasiloxane-α,ω-diol could form in the environment. Based on the above ratio of the rate constants, it is possible that the concentration of D4 is 6.7 times that of the octamethyltetrasiloxane-α,ω-diol, but that the concentration of octamethyltetrasiloxane-α,ω-diol (and hence D4) declines further as it itself degrades. The net result may be that the effective hydrolysis half-life of D4 in the environment is similar to that above in the early stages of the process (where the concentration of D4 is the highest), but it could be longer than indicated above in the latter stages of the degradation curve. This is dependent on several factors, notably the actual concentration of octamethyltetrasiloxane-α,ω-diol in the environment and its own rate of hydrolysis, and it is currently difficult to predict.

A study to investigate the stability of D4 in natural lake sediments under laboratory conditions is currently underway. The results from a preliminary study recently became available (CES, 2006; Kozerski *et al*., 2007). The study was carried out under static conditions in open containers and was designed to determine the contribution of the volatile loss and degradation (hydrolysis) to the total loss of D4 from the system.

The two natural sediments used in the study were collected from a lake and a river upstream of the lake in Michigan, USA. Sediment 1 was a sandy one that consisted of 80 per cent sand, 16 per cent silt, and 4 per cent clay, with an organic carbon content of 1.11 per cent. It was collected at a water depth of around 3.5 m from a lotic environment (upstream of the lake). Sediment 2 was a sandy-silt that consisted of 42 per cent sand, 44 per cent silt, and 14 per cent clay, with an organic carbon content of 2.95 per cent. It was collected at a water depth of about 7.6 m from an open-water lentic environment at the widest and deepest part of the lake. Overlying water from the same location as the sandy–silt sediment was used in the study (the pH of the water was 8.0–8.2 in both cases).

^{14}C-D4 was tested (no information was given on the radiochemical purity of the substance tested). The test chambers consisted of glass jars (surface area ~20 cm^2) that contained 18 cm^3 of sediment and 90 cm^3 of overlying water (water volume to sediment volume ratio of 5:1). The jars were then shaken to disperse the sediment before adding the test substance. ^{14}C-D4 was dosed to the jars as a solution in *N*,*N*-dimethylformamide (DMF). A total volume of 100 µl of the DMF solution was added to each jar. The initial nominal concentration of D4 in the final sediment was 0.5 mg/kg wet weight (~1 mg/kg dry weight). After addition of ^{14}C-D4, the sediments were allowed to settle for one hour and the initial concentration of the test substance then determined. The jars were left uncapped with minimal disturbance and incubated at 20–25°C for up to 120 days. Deionised water was added as needed to replenish water loss through evaporation. Samples of sediment were collected for analysis at various time periods.

At each sampling point, triplicate jars were sacrificed (except for sediment 2 at day 120, where only one jar was available) and the total concentration of ^{14}C in the sediment solids, pore water, and overlying water determined. The ^{14}C present in overlying water and pore water is assumed to represent D4 and water-soluble degradation (hydrolysis) products of D4. The fraction of the initial ^{14}C not accounted for in these phases is assumed to be lost from the test system by volatilisation (either as D4 or as volatile degradation products).

The results obtained from the two sediments are broadly similar. Around 40 per cent of the total ^{14}C is estimated to be lost by volatilisation over the 120 day test period. A significant decrease in the fraction of ^{14}C associated with the sediment phase occurred in the experiment, with a concomitant increase in the amount of ^{14}C in the water phase (assumed to be water-soluble degradation products). In addition to ^{14}C measurements, the sediment solids were also analysed for D4 by solvent extraction followed by HPLC analysis on days 7, 43, and 84. These analyses confirmed that the main species in the sediment solids was D4

(the method used is thought to be able to detect metabolites at around 10 per cent or more of the concentration of D4).

The decrease in the total ^{14}C activity associated with the sediment solids (normalised to the amount at day 0) is shown in Figure 3.1.[12] The figure also shows the hypothetical first-order loss curves that correspond to half-lives in sediment of 120 days and 180 days [the two cut-offs that are important for the persistent, bioaccumulative, and toxic (PBT) and very persistent, very bioaccumulative (vPvB) assessment; see Section 5.5.2.

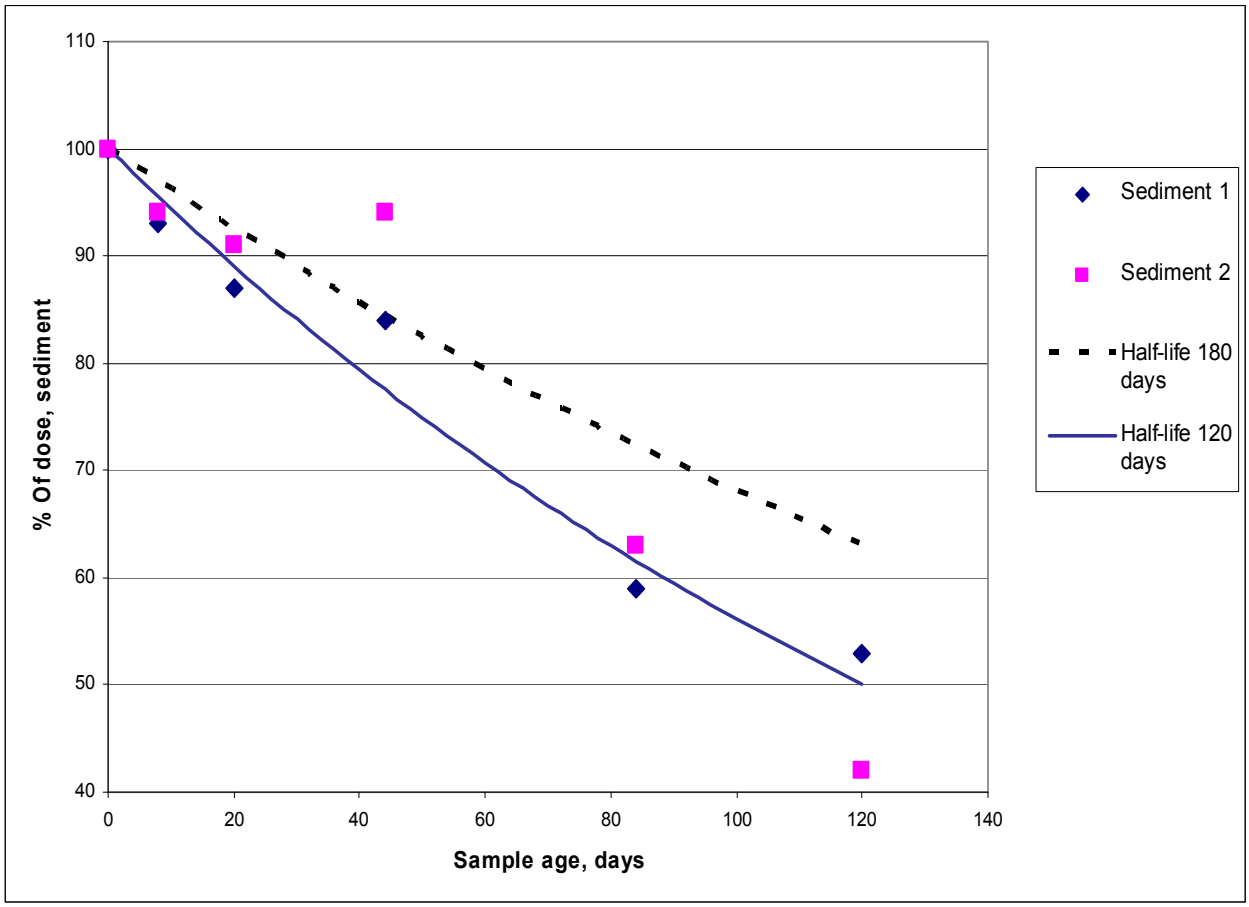

Figure 3.1 Decrease in 14C activity with time in sediment (CES, 2006; Kozerski et al., 2007)

Figure 3.1 shows that the disappearance half-life of ^{14}C from the sediment is close to 120 days in this experiment. Based on these data, Kozerski *et al*. (2007) estimated the half-life for disappearance of ^{14}C from the test system (assuming a first-order process) to be around 131 days in sediment 1 (sandy sediment) and 115 days in sediment 2 (sandy–silt sediment)

These experiments were carried out at 20–25°C and it is possible that the half-lives at the lower temperatures assumed in the TGD (typically 12°C for the freshwater environment and 9°C in the marine environment) could be longer than 120 days (but it is not yet possible to correct for this).

Although the half-life figures given are based on the amount of ^{14}C in the sediment (and so could include both metabolites and D4), the available limited analysis carried out shows that

[12] The data in CES (2006) and Kozerski *et al*. (2007) are presented diagramatically only. The figure is reconstructed here using the approximate values taken from the diagrams given in the original publications.

a large proportion of the ^{14}C in the sediment phase was as parent D4 and so the half-life values effectively represent the loss of D4 from the sediment phase. As this is a preliminary study the results should be treated with caution.[13]

3.2.2.3 Photolysis

No information is available on the direct photolysis of D4 in water.

3.2.2.3 Biodegradation

No significant biodegradation is reported for D4 in an unpublished five day closed bottle biological oxygen demand test carried out using a D4 concentration of 500 mg/l (IUCLID, 2005). No further details of this test are available.

Springborn Smithers Laboratories (2005) studied the biodegradability of D4 using the draft OECD 310 methodology [ready biodegradability – CO_2 in sealed vessels (headspace test)]. The D4 tested was 99.7 per cent pure and sodium benzoate was used as a reference substance in the test. The inoculum was derived from activated sludge and sewage from a WWTP that received primarily domestic waste, and soil from a wooded area. The inoculum was added to the test medium at a concentration of 10 mg solids/l, D4 was added at a concentration of 10 mg carbon/l and incubated in the dark at 22 ± 2°C. At intervals during the test the amount of CO_2 (measured by total carbon analysis) in the headspace was determined (three replicates were sampled on each occasion). A control (inoculum only), positive control (which contained sodium benzoate at a concentration of 10 mg carbon/l), and toxicity control (which contained sodium benzoate and D4, both at a concentration of 10 mg carbon/l) were also run.

The test showed 3.7 per cent degradation of D4 at day 29 of the test period (the maximum degradation was 16.2 per cent at day 21). The degradation in the positive control was 104 per cent after 29 days (with >60 per cent degradation within the 10-day window), which indicates that the inoculum used was viable, and the toxicity control showed that D6 was not toxic to the microorganisms present. The solubility of D4 is limited (0.056 µg/l) and so it is possible that this may have limited the bioavailability of D6 in this test. In addition, it is possible that D4 itself could have been in the headspace [the OECD 310 guideline suggests that this could be significant for substances with a Henry's law constant >50 Pa m^3/mol and that for D4 is well above this value (1,214,000 Pa m^3/mol at 25°C)], and so could have contributed to the carbon measured in the headspace. Overall, based on these results, D4 is not considered to be readily biodegradable.

The biodegradation of D4 was investigated using pure bacterial cultures isolated from activated sludge from various WWTPs. The study is an unpublished study, but a summary of the results is given in IUCLID (2005). The test was carried out using ^{14}C-D4, which was added (concentration of 10 mg/l) to 50 ml of cell suspension and the cells incubated at ambient temperature for one week. Biodegradation was reported to occur with cells derived from WWTPs that had been acclimated to nitrogenous wastes. Complex silanols were

[13] IThe Kent *et al.* (1996) study reported in Section 0 could be interpreted as showing a much more rapid removal from sediment by volatilisation in a different test system. However, there are problems in interpreting the Kent *et al.* (1996) study in this respect, notably that the 'volatiles' were extracted from the sediment–water system by passing CO_2-free air through the system over three days. Also, the concentrations in sediment were not determined in this study and so there is no information on the half-life in the sediment phase itself.

tentatively identified as the degradation products. The degradation appears to be linked with the formation of nitrous oxide by the oxidation of ammonia or via denitrification. No further details of this study (in particular relating to the precautions taken to avoid loss from volatilisation) are currently available.

Kent *et al.* (1996) studied the biodegradation of D4 in sediments using an aerobic microcosm system. The test system consisted of natural sediment and water collected from an uncontaminated pond. The sediments were passed through a 2 mm sieve prior to use. The experiments were carried out by adding ^{14}C-D4 directly to the aqueous phase of the system (nominal concentration 30 µg/l) and the rate of mineralisation and disappearance of the test substance followed over 56 days. Sterile control sediments were also used. Volatile products were collected over a ten minute period once every three days by passing CO_2-free air through the system and collecting the products on a volatile organic trap and a CO_2 trap. This pattern of aeration–product collection was used to minimise the loss of D4 through volatilisation from the system while maintaining adequate aerobic conditions for the microbial population. Essentially no biodegradation was observed in this system. The majority of the D4 added to the chamber was lost from the system through volatilisation (i.e. it was collected on the volatiles trap). Less than 5 per cent of the total radioactivity remained in the water and sediment after 28 days. A small and variable amount of radioactivity (typically <10 per cent of the total added) was found in the CO_2 traps of both the viable sediments and the sterile (abiotic) controls. This radioactivity was traced to products of alkaline hydrolysis of D4 (formed on the volatiles trap as a result of contamination of the trap by potassium hydroxide from the following CO_2 trap) rather than from biodegradation products of D4. Overall, Kent *et al.* (1996) conclude that D4 was lost from the system through volatilisation, with no evidence for biodegradation. The original test report (Fackler, 1991) for this study has since been obtained and evident short-comings are (Maycock *et al.*, 2005):

- The mass balance was often poor and variable (ranged between 47.3 and 101.6 per cent, with many values below 80 per cent).
- The amount of 14C measured in the sediment was very variable in replicates for the same time point.
- The paper assumed that hydrolysis occurred in the volatiles trap because of backflow into the trap of potassium hydroxide from the CO2 trap. Although it was shown that a similar product could be formed from D4 under basic hydrolysis conditions, and that this product of basic hydrolysis was of low volatility and so unlikely to be purged from the test chamber into the trap during the study, it is still possible that a genuine degradation product was actually detected in the trap.

Therefore it is difficult to draw firm conclusions on whether or not degradation of D4 occurred in this study as the variability and uncertainty in the results is too high.

In an unpublished study no biodegradation is reported when ^{14}C-D4 is incubated at a concentration of 30 µg/l in a water sediment system for 42 days under aerobic conditions. A summary of the results is given in IUCLID (2005), but it is likely that this study is the same study reported above by Kent *et al.* (1996).

Grümping *et al*. (1999) studied the anaerobic biodegradation of D4 studied using a digested sewage sludge inoculum. The sewage sludge was from a municipal WWTP in Germany fed mainly with domestic sewage. The experiments were carried out using 100 ml bottles that contained 50 ml of sewage sludge spiked with 100 mg/l of D4 and a CO_2 and hydrogen (ratio 20:80) atmosphere. The bottles were incubated in an anaerobic chamber at 37°C in the dark for up to 100 days. Sterilised control sludge samples were used as the control. The degradation product dimethylsilanediol formed during the experiment. The maximum amount of dimethylsilanediol after 100 days corresponded to around 3 per cent of the D4 initially

added to the system. With further incubation of the system the concentration of dimethylsilanediol decreased over a subsequent two month period, possibly through biodegradation. No dimethylsilanediol was detected in the sterile control. Although these results indicate that D4 undergoes anaerobic degradation it is difficult to determine the significance of this process in the environment from them because:

- a very high inoculum concentration was used;
- the headspace in the incubation flasks was around 50 ml, which means a significant fraction of the D4 added was likely to be in the headspace and so not available for biodegradation;
- the concentration of D4 initially added was well in excess of the substance's solubility in water, which again means a substantial fraction of the D4 added was not available for biodegradation;
- no data are reported on the concentrations of D4 itself during the test.

Accettola *et al.* (2008) isolated bacteria from activated sludge that were able to grow under aerobic conditions when D4 in the headspace was the only source of carbon. In the experiment, batch cultures were prepared using a mineral medium and D4 added either directly to the mineral medium (4 ml of D4 in 150 ml of medium) or by a separate container within the culture flask (in this case the only route to the water phase was via the headspace). The cultures were inoculated with either a pure strain of *Pseudomonas putida*, activated sludge from a municipal WWTP, or activated sludge from an industrial WWTP of a company that produced silicones. The cultures were incubated under aerobic conditions with shaking and the growth of the bacteria monitored. At intervals, the cultures were re-inoculated into fresh media. Growth of bacteria was apparent over 79 days in the cultures inoculated with either municipal or industrial activated sludge when D4 was available only via the headspace. Analysis of the medium for degradation products indicated the presence of dimethylsilanediol (it is possible that this could be formed from the hydrolysis of D4 rather than by biodegradation).

3.2.3 Degradation in soil

Xu (1999) investigated the degradation of D4 in soil. The study was designed to analyse the significance of all possible degradation pathways, including ring-opening polymerisation reactions (essentially to form PDMS), demethylation reactions, and hydrolysis reactions.

The soil used in the study was the Wahiawa Series from the Kunia area, Hawaii, and it was air-dried before use. The tests were carried out using ^{14}C-D4 (radiochemical purity >99 per cent) and the chemical dissolved in pentane prior to spiking the soil. The tests were carried out in Teflon® tubes that contained either 1 g or 5 g of soil. The 0.25 ml of the pentane solution of D4 was then added to the soil, and the tube flushed with air for two minutes. The initial target D4 concentrations were in the range 40–200 mg/kg dry weight. The spiked soil was then incubated in the closed tubes in the dark at room temperature for between ten minutes and seven days. At the end of the incubation period the soils were solvent extracted and the D4 that remained and degradation products determined. To simulate the effects of a rainfall event, similar experiments were also carried out using soil that was wetted (3 ml of saturated $MgSO_4$ solution added to 1 g of dried soil) after 45 minutes incubation. The overall recovery of total ^{14}C in the study was good (e.g. it ranged between 94.5 and 101.2 per cent at four sampling periods over seven days for the $MgSO_4$ experiment).

The results show no evidence for the ring-opening polymerisation of D4 at concentrations <200 mg/kg dry weight, although small amounts of D5 and D6 were thought to form in some experiments at high humidity (100 per cent relative humidity). Therefore it is concluded that no significant polymerisation of D4 to PDMS occurred in soils at concentrations <200 mg/kg dry weight. Similarly, no evidence shows that D4 degraded by demethylation reactions.

D4 hydrolysed rapidly in the experiments with dry soil to form more polar products. For example, around 50 per cent of the D4 disappeared and five hydrolysis products were evident after 0.5 hours incubation, and by 24 hours only two main hydrolysis products remained. The reaction proceeded via ring-opening hydrolysis to form the linear octamethyltetrasiloxanediol (tetramer diol), with subsequent loss of dimethylsilanol to form the hexamethyltrisiloxanediol (trimer diol), tetramethyldisiloxanediol (dimer diol), and eventually dimethylsilanediol.

The experiments with wet soil showed the same intermediate and final degradation products were formed. However there was evidence that some of the intermediate diols condensed to form larger cyclic siloxane oligomers such as D3 and D4.

According to Xu (1999), earlier studies show that dimethylsilanediol (the final degradation product of D4) is lost from soil by volatilisation and biodegradation. The ultimate biodegradation products from dimethylsilanediol are likely to be CO_2 and silica (Chandra, 1997). In addition, any dimethylsilanediol lost from the soil by volatilisation may further degraded to CO_2 and silicic acid and/or silica in the atmosphere. This, therefore, provides a complete degradation pathway for D4 in soil.

Xu and Chandra (1999) carried out more experiments on two soils to better establish the rate of degradation and volatilisation of D4 from soil. Two soils were used in these experiments. One was a typical temperate soil (coarse-textured alfisol), with a pH of 7.6 and organic matter content of 2.4 per cent, and consisted of 50 per cent sand, 28 per cent silt, and 22 per cent clay. The predominant clay minerals in this soil were illite and chlorite. The second soil was a highly weathered soil (a clay oxisol), with a pH of 4.9 and organic matter content of 2.2 per cent, and consisted of 21.2 per cent sand, 24.0 per cent silt, and 54.8 per cent clay. The predominant clay minerals present in this soil were kaolinite, gibbsite, and goethite.

^{14}C-D4 (radiochemical purity >99 per cent) was tested. The degradation experiments were carried out using sealed systems under different relative humidities (32, 92, and 100 per cent). The soils were prepared by pre-equilibrating samples of 5 g of air-dried soil in 30 ml Teflon® tubes to the required relative humidity atmosphere in a desiccator. After a seven day pre-equilibration period the soil was spiked with the ^{14}C-D4 as a solution in pentane (the amount of D4 added is equivalent to an initial soil concentration of ~40 mg/kg dry weight) and the tube was immediately capped. After two minutes the cap was removed and the tube flushed with air of the correct humidity for 90–120 seconds to evaporate the solvent. After this the tubes were recapped and incubated at 22°C for between 0 and 21 days. The experiments to investigate the volatilisation loss were prepared in a similar way, but incubated without capping.

At various times the amount of ^{14}C-D4 in the soil was determined. D4 degraded in the test system, and the rate increased as the relative humidity decreased. The rate of degradation was also generally faster in the weathered soil than in the temperate soil. The degradation half-lives are around 0.89 days (21 hours), 0.08 days (1.9 hours), and 0.04 days (58 minutes) in the weathered soil at relative humidities of 100, 92, and 32, respectively, and 5.25 and 3.54 days in the temperate soil at relative humidities of 92 and 32 per cent (little or no degradation of D4 occurred in the temperate soil at 100 per cent relative humidity). The total recovery of ^{14}C in this study was good (ranged between 94.5 and 101.2 per cent, with an average of 98.7 per cent, when ^{14}C-D4 was incubated for 0.25–7 days in soil at 32–100 per cent relative humidity).

The degradation is thought result from hydrolysis reactions catalysed by the surface activity of soil clays. The increase in moisture of the soil is thought to decrease the surface acidity and thus the hydrolysis rate. The differences in degradation rates obtained in the weathered soil compared with those of the temperate soil occurred because the weathered soil had a higher clay content, and the clay minerals in this soil were kaolinite (around 50 per cent of the clay minerals) and gibbsite (around 10 per cent of the clay minerals), both of which are highly effective catalysts of PDMS. In contrast, as well as having a lower clay content, the clay minerals in the temperate soil were illite and chlorite (the former is one of the least-effective catalysts for hydrolysis of Si–O–Si linkages).

The volatilisation experiments show that loss through volatilisation from soil is a significant competing process for D4 in soils in open systems. At a relative humidity of around 50 per cent, volatilisation accounts for around 40 per cent of the total loss of D4, but loss by volatilisation is negligible compared to that from degradation in dry soils

(relative humidity 32 per cent). In soils at high relative humidity (~100 per cent) loss through volatilisation is the dominant removal process (e.g. 80 per cent loss through volatilisation over the incubation period compared with 5 per cent by degradation).

Earlier, Buch and Ingebrigtson (1979) studied the degradation of D4 (and PDMS) in soil. The dried soils (representative soils from Michigan) were ground and sifted through an 80-mesh screen (the soils were generally dried at 80°C for seven days, but in some cases at 105°C for two hours or for 14 days at room temperature). The soils were then rehydrated to specific moisture contents by storing the dried soils in dedicators at constant humidities of 0, 20, 45, and 98 per cent for 4–6 weeks.

Tests were carried out to investigate the degradation of a number of ^{14}C-labelled substances, including D4, PDMS fluids with a range of viscosities, and linear siloxane oligomers (e.g. dodecamethylpentasiloxane).

To study the interaction of the soils with the chemical the substance was added as a solution in methyl isobutyl ketone, the solvent evaporated and then the soil mixed with the test substance in a sealed polyethylene bottle. The mixed soil was then stored at a constant temperature and the amount of test substance present was determined at various times. The volatile and non-volatile products formed were also collected and determined (the experiment was carried out under a flow of air, and the volatiles were collected on a charcoal trap).

The half-life for PDMS (initial concentration 6000 mg/kg soil) in the experiments using Iowa top soil was around 30 days (no details of the temperature are given). The degradation products are thought to consist of lower molecular weight siloxane species. Under similar conditions, D4 was also found to degrade and form cyclic oligomers (D5 and D6) and hydroxyl end-blocked linear oligomers.

To determine the factors that affect the degradation, several different soils at different moisture levels were tested. The temperature and moisture content of the soil affected the ability of the soil to degrade PDMS, D4, and linear siloxane oligomers. The rate of degradation increased as the moisture content decreased and temperature increased. In addition, soils with higher clay contents were generally more active in the degradation of PDMS-based products. The degradative activities of several clay types were investigated (initial PDMS concentration 10,000 mg/kg). The activity of clays also depended on the moisture content of the soil (the rate of degradation again being faster in drier soils). Kaolinite no. 9, halloysite no. 29, halloysite no. 13, and montmorillonite no. 27 all showed activity for degrading linear siloxane oligomers, but the degradation of cyclic siloxane oligomers (e.g. D4) was significantly slower with montmorillonite no. 27 and halloysite no. 29 than with the other clay minerals tested.

3.2.4 Evaluation of environmental degradation data

3.2.4.1 Abiotic degradation

Degradation of D4 occurs in the atmosphere by reaction with atmospheric hydroxyl radicals. Hydrolysis of D4 can also occur under acid, neutral, and alkaline conditions.

In terms of the environmental risk assessment, the TGD recommends that a pH of 7 and a temperature of 12°C are used for the freshwater environment. For the marine environment a higher pH (around 8), but lower temperature (around 9°C) are considered. The relevant hydrolysis half-lives under these conditions are summarised in Table 3.7.

Table 3.7 D4 half-lives for freshwater (pH 7) and the marine environment (pH 8)

Temperature (°C)	pH	Hydrolysis half-life (days)
12°C	7	16.7
9°C	8	2.9

Gerhards (2005) reviewed the pH of water in the major water courses in the EU. The analysis focussed on the major European catchment areas which transport the (treated) wastewater of approximately 285 million people (i.e. over half of the total EU population of 450 million people). The pH of all rivers included in the survey was in the range 7.57–8.36, most with a pH close to 8.0. When the discharge volume is used as a weighting factor, the average pH of the waters is 7.9. The relatively high overall pH is thought to result from the widespread installation of equipment to remove sulphur dioxide from electric power generation plants, which in turn has reduced 'acid rain' and lead to a slow increase in the overall pH of surface water. For marine waters, the pH of the North Sea varies between 7.9 and 8.4, with an average value of 8.2. As the estimates above show, the hydrolysis half-life of D4 around a pH of 8 is very short.

In summary, the following abiotic half-lives are assumed in this assessment.

- atmospheric photo-oxidation, 14 days
- photodegradation in air, infinite
- photodegradation in water, infinite
- hydrolysis (pH 7, 12°C), 16.7 days
- hydrolysis (pH 8, 9°C, marine), 2.9 days.

3.2.4.2 Biodegradation

Overall, the available standard biodegradation experiments show little evidence that D4 is biodegradable. However, D4 is highly volatile, and will partition readily into the air from water, which thus makes it unavailable to the microorganisms in the test systems used. Therefore to test for biodegradation of D4 is very difficult. For example, it is likely that a major proportion of D4 was in the headspace in the tests rather than in the water phase. Thus, although the available data appear to indicate that D4 is not readily biodegradation, they do not provide absolute proof that the substance is not biodegradable.

Degradation of D4 occurs in dry soils (most probably by an abiotic mechanism). However, moisture significantly reduces the rate of degradation, such that when the dried soil is equilibrated with a 100 per cent relative humidity atmosphere there is essentially no degradation. In terms of the environment, although dry soils may exist in some situations (e.g. drought), most soils contain moisture, and even dry soils are exposed to moisture in the air [as simulated in the studies by Xu (1999) and Xu and Chandra (1999)]. Thus, although it is possible that such degradation in soils could occur under some circumstances in the environment (low relative humidity drought conditions) this is unlikely to be the typical case. Furthermore, one of the main soil compartments relevant to the risk assessment is

agricultural soil. Here crops are likely to be watered during dry conditions and so the degradation under such conditions is likely to be limited.

Xu (personal communication) carried out a further analysis of the soil degradation data for D4, as reported by CES (2005b) and Xu (2007a). The analysis is based on the data of Xu and Chandra (1999) and uses the assumptions:

- the ratio of degradation rates of the various cyclic VMSs relative to D4 are the same at any given moisture level in different soils;
- the rates of degradation of any given cyclic VMS are linearly related to water potential [which is, in turn, linearly related to log relative humidity as measured with Londo soil].

The estimated half-lives of D4 in a temperate and tropical soil using this approach are summarised in Table 3.8 [the Xu and Chandra (1999) study was carried out at 22°C].

Table 3.8 D4 half-lives for temperate and tropical soils

Relative humidity (%)	Half-lives (days)	
	Temperate soil	Tropical soil
50	4.1 days	0.05 days
70	4.7 days	0.06 days
90	5.3 days	0.08 days

The half-lives in Table 3.8 relate to a dry soil exposed in air of the stated relative humidity. CES (2005b) indicates that, for comparison, the water content of Londo soil [as used by Xu and Chandra (1999)] in the 32.5 per cent relative humidity experiment is 2.1 per cent.

Xu (personal communication) used similar assumptions to those above and estimated a half-life of 2.3 days for a typical soil in the dry season in France [as reported in CES (2005b)]. In France the soil moisture content may regularly decline to between 5 and 10 per cent during the summer months.

The degradation in the soil studies with cyclic siloxanes parallels that of PDMS (see Section 0). The degradation of PDMS is also dependent on the soil moisture content (among other factors) and, although degradation generally slows as the water content of the soil increases, it still occurs. For representative soils, significant degradation of PDMS occurs over periods of several months to a year under field conditions (with half-lives of the order of 1000 days estimated in one set of experiments). The similarity of the mechanisms of degradation of PDMS and D4 implies that degradation of D4 still occurs in wet soils. The available studies on cyclic siloxanes do not provide any direct evidence of this as volatilisation becomes the most dominant removal mechanism from moist soil in the experiments carried out (i.e. all the D4 is lost from the soil before degradation can occur).

The main degradation product of D4 in soils is eventually likely to be dimethylsilanediol. This is expected to undergo further degradation processes in the environment and ultimately form CO_2 and silica and/or silicic acid, and so provides a complete mineralisation pathway for D4 in soils where such degradation occurs.

In terms of this assessment, it is assumed that D4 is not biodegradable as a worst case. However, in the environment it is likely to be removed from aquatic and terrestrial systems by volatilisation into the atmosphere. Removal by volatilisation is built into the PEC calculations for both water (at a regional level only) and soil (at a local and regional level). To reflect the evidence that D4 is also removed from soil by degradation, the effect of including example

degradation rates (e.g. assuming half-lives of six months, one year, and ten years at 12°C, as well as of 2.3 days at 22°C, as estimated above for a typical soil in the dry season in France) on the resulting PEC calculations is investigated (see Section 0).

Also, under some conditions (e.g. particularly dry spells) the degradation of D4 in soil could become very rapid (and become the dominant removal process from the soil). However this does not represent a realistic worst-case situation, as explained above.

3.2.5 Environmental partitioning

3.2.5.1 Adsorption coefficients

Calculated values

A value for K_{oc} of 18,000 l/kg can be estimated for D4 from its chemical structure using the USEPA EPI (v3.12) estimation software.

Chandra (1997) uses four different correlation equations (which relate the K_{oc} to water solubility or log K_{ow}) to estimate K_{oc} for D4. The mean value for the estimated K_{oc} is 14,800 l/kg.

The partition coefficients in Table 3.9 are estimated using a log K_{ow} value of 6.49 and the methods outlined in the TGD. The equivalent values obtained using a log K_{ow} of 5.1 are also shown.

Table 3.9 Partition coefficients for D5 using K_{ow} values of 6.49 and 5.1

	log K_{ow} 6.49	**log K_{ow} 5.1**
Organic carbon–water partition coefficient (K_{oc})	2.3×10^5 l/kg	1.7×10^4 l/kg
Solids–water partition coefficient in soil (K_{soil})	4.6×10^3 l/kg	340 l/kg
Solids–water partition coefficient in sediment (K_{sed})	1.1×10^4 l/kg	850 l/kg
Solids–water partition coefficient in suspended matter (K_{susp})	2.3×10^4 l/kg	1.7×10^3 l/kg
Soil–water partition coefficient ($K_{soil–water}$)	6.9×10^3 m^3/m^3	610 m^3/m^3
Suspended matter–water partition coefficient ($K_{susp–water}$)	5.7×10^3 m^3/m^3	430 m^3/m^3
Sediment–water partition coefficient ($K_{sed–water}$)	5.7×10^3 m^3/m^3	430 m^3/m^3

Experimental values

A recent, high-quality, study was undertaken by industry on a voluntary basis to investigate the actual K_{oc} value for D4. The study was carried out in accordance with Good Laboratory Practice (GLP) using the OECD 106 batch equilibrium method (Miller, 2007). Earlier draft versions of this risk assessment show the importance of K_{oc} to the assessment of the affects of D4 in the sediment compartment in particular, and the study was undertaken to address the uncertainties in this endpoint.

^{13}C-D4 of 99.8 per cent purity was used. ^{13}C-D5 facilitates the analysis of low levels of D4 in the water phase (enriched ^{13}C-D4 has an inherently lower analytical background than unlabelled D4).

Three soils were used in the study. These were collected from the UK and covered a range of organic carbon contents (2.0–5.5 per cent) and pH values (pH 5.5–8.3). The properties of each soil used are summarised in 10.

A number of experiments were carried out to investigate the effect of the soil:water ratio and equilibration time on K_{oc}. These were used to determine the optimum conditions for the definitive adsorption isotherm studies.

Table 3.10 Properties of soils used in the K_{oc} determination for D4 (Miller, 2007)

Property		Soil		
		Silty loam	Sandy loam	Sandy-clay loam
Soil pH		6.6	5.5	8.3
Organic carbon content (per cent weight by weight)		3.4	2.0	5.5
Cation exchange capacity [milliequivalent (meq)/100g)]		18.0	9.9	20.4
Water-holding capacity (per cent weight by weight)		41.1	16.4	31.4
Composition (per cent by weight)	Sand	22	72	61
	Silt	56	13	19
	Clay	22	15	20

The methodology used was similar in all cases. Each experiment was carried out in duplicate. Briefly, the required amount of test soil (see below) and approximately 25 g of 0.01 M $CaCl_2$ solution were added to the test vessel (a glass tube fitted with a screw cap). The soil–water mixtures were mixed overnight on a rotational mixer. The experiments were initiated by the addition of 25 µl of a solution of ^{13}C-D4 in N,N-DMF.[14] The solution was added to the soil–water mixture via a valve in the screw cap. The test vessel was then returned to the mixer and incubated at constant temperature for the required time. The average temperature during the experiments was 24.8°C (standard deviation ±0.1°C). At the end of the incubation period, the levels of ^{13}C-D4 in both the aqueous and solid phases were determined. The analytical methodology used was subject to an extensive quality-assurance and quality-control procedure to minimise the influence of analytical artefacts in the concentrations measured. Checks were also made to ensure that the test substance was stable during the determinations and that adsorption onto the surface of the test vessel was not significant.

The first set of studies was designed to determine the optimal soil:solution ratio. These were carried out using the silty loam at three different soil:solution ratios of 1:10, 1:20, and 1:50 weight by weight. The test vessels were spiked with 1000 ng ^{13}C-D4 per tube and equilibrated for half, one, two, four, six, 24, or 30 hours. Equilibrium was reached by 24 hours, and the log K_{oc} values determined after 24 hours were similar at the three soil:solution ratios (mean log K_{oc} = 4.13 at the 1:10 ratio, 4.17 at the 1:20 ratio, and 4.19 at the 1:50 ratio). As the impact of the soil:solution ratio on the K_{oc} was minimal, a soil:solution ratio of 1:20

[14]The amount of N,N-DMF in the test vessel was 0.1% volume/volume of the aqueous phase, which is consistent with the limit stated in the test guideline.

was used in all subsequent experiments because this facilitated the analysis of the water phase.

The next series of experiments investigated the time to equilibrium in the sandy loam and sandy–clay loam soils using a soil:solution ratio of 1:20 spiked with 1000 ng ^{13}C-D4 per tube. Equilibrium was again reached rapidly (approaching equilibrium within 30 minutes) and the mean log K_{oc} values determined after 24 hours were 4.19 for the sandy loam and 4.25 for the silty–clay loam.

Desorption experiments were also carried out for all three soils by placing the solid phase in fresh $CaCl_2$ after equilibrium had been reached and monitoring the re-attainment of equilibrium. The desorption equilibrium was rapidly attained (within 30 minutes) and the mean log K_{oc} was determined as 4.28 for the sandy loam, 4.23 for the silty loam, and 4.35 for the sandy–clay loam.

The definitive experiments determined the adsorption isotherms in each soil. These experiments used a soil:solution ratio of 1:20 and a range of ^{13}C-D4 concentrations (the nominal spiked amounts were between 10 and 1000 ng/tube). The K_{oc} value was determined after 24 hours of incubation. The K_{oc} data were evaluated using the Freundlich equation. The adsorption isotherms are linear over the concentration range studied and the mean log K_{oc} values determined (± standard deviation) are 4.22 ± 0.01 for the sandy loam, 4.17 ± 0.01 for the silty loam, and 4.27 ± 0.03 for the sandy–clay loam. The overall average log K_{oc} value from these experiments is 4.22 ± 0.01.

The final series of experiments determined the desorption isotherms using the same six nominal concentrations of ^{13}C-D4. In these experiments, the test vessels were spiked with the ^{13}C-D4 and equilibrated for 24 hours. After which the aqueous phase was removed, fresh $CaCl_2$ added, and the vessel incubated for a further 24 hours. The K_{oc} values were then determined and evaluated using the Freundlich equation.

The desorption isotherms are linear over the concentration range studied and the mean log K_{oc} values determined (± standard deviation) are 4.27 ± 0.02 for the sandy loam, 4.23 ± 0.02 for the silty loam and 4.39 ± 0.01 for the sandy–clay loam. The overall average log K_{oc} value from these experiments is 4.30 ± 0.08. When compared with the values obtained in the adsorption isotherm experiments, there is a small, but systematic, increase in the log K_{oc} obtained, which suggests only a minor apparent irreversibility in the adsorption–desorption of D4 for short contact times. However, adsorption to natural particles is a complex process, and the short contact times used in this study may favour faster sorption processes over other processes that could occur in the environment over longer timescales.

Overall, this is a high-quality study with reproducible results over a range of experimental conditions for three different soils. The mean log K_{oc} of 4.22 from the adsorption isotherm experiments is used in the risk assessment. This is equivalent to a K_{oc} of 1.7×10^4 l/kg.[15]

Summary of adsorption coefficients used in the risk assessment

The K_{oc} value is taken as 1.7×10^4 l/kg. The partition coefficients used in the assessment (estimated from the K_{oc} value using the methods outlined in the TGD) are:

- Koc, 1.7 × 104 l/kg

[15] In the original test report the K_{oc} values are determined given dimensionless values as the concentration in the aqueous phase was determined in terms of the mass (rather than volume) of solution. As the density of 0.01 M $CaCl_2$ solution is close to 1 kg/l, the dimensionless K_{oc} is numerically equivalent to a value with units of l/kg (this is the form used in the methodology in the TGD).

- Ksoil, 340 l/kg
- Ksed, 850 l/kg
- Ksusp, 1.7 × 103 l/kg
- Ksoil–water, 610 m3/m3
- Ksusp–water, 430 m3/m3
- Ksed–water, 430 m3/m3.

3.2.5.2 Behaviour in wastewater treatment plants

Mueller *et al.* (1995) used a sewage treatment plant model to estimate the percentage removal during treatment. The total removal of D4 was predicted to be around 82 per cent, of which volatilisation to the atmosphere accounted for 36 per cent and adsorption to sludge accounted for 46 per cent.

Parker *et al*. (1999) investigated the behaviour of D4 during wastewater treatment using a pilot-scale municipal activated sludge. WWTP The overall removal of D4 from the system is 86.4 per cent, but they report that the overall mass balance for the chemical in the experiment is generally low. Modelling experiments indicate that the low mass balance is probably caused by an underestimation of the removal by primary sludge that results from the sampling method used (grab samples were taken, which may not accurately reflect the high variability of the suspended solids concentration in the primary influent suspended solids concentration). When this underestimation is taken into account it appears that loss via volatilisation and loss by adsorption onto sludge solids contributes approximately equally to the total removal.

The expected behaviour of D4 during wastewater treatment is estimated using the Simpletreat model within EUSES 2.0.3 and gives the distribution as:

- percentage to air, 48.2
- percentage to sludge, 48.2
- percentage degraded, 0
- percentage to water, 3.55.

Therefore the overall removal predicted is around 96.4 per cent. These values are in reasonable agreement with the results from Parker *et al*. (1999) and are used in the subsequent PEC calculations.

3.2.6 Adsorption

The K_{oc} for D4 is estimated as 1.7×10^4 l/kg, which means that D4 adsorbs strongly to sediment and soil. Given that it is also of very low water solubility and highly volatile, leaching from soil is not expected to be a significant process in the environment.

3.2.7 Volatilisation

Hamelink *et al*. (1996) studied the volatilisation rate constant of D4 from water. The test was carried out using 1600 ml of pure water in a 2 litre beaker at 20°C. Before use, the water was de-oxygenated (dissolved oxygen content of <1 mg/l) by bubbling nitrogen through it. The water was then stirred at a constant speed (the rate of stirring was used to vary the re-aeration rate of the water for different experiments), D4 added (as a solution in methanol; the actual concentration of D4 added is not given but appears to be below the water solubility limit), and the concentration of D4 in the water phase determined at various times (at least ten sampling points for each experiment). In addition, the re-aeration rate was determined by measuring the dissolved oxygen concentration of the water. Both the volatilisation rate constant for D4 and re-aeration rate constant of the water increased with increasing speed of stirring, but the ratio of the volatilisation rate constant to the re-aeration rate constant did not vary with stirring speed (the mean value was 0.57 ± 0.17). Based on these results, and knowledge of typical re-aeration rates of water bodies, the half-life for volatilisation of D4 is estimated as between three and 138 hours for rivers and 138 and 345 hours for lakes and ponds.

Another estimate for the volatilisation rate from water is obtained using the USEPA EPI estimation program. With a Henry's law constant of 1.21×10^6 Pa m^3/mol the volatilisation half-life for D4 is estimated as 1.8 hours in a river (the estimate assumes the river has a depth of 1 m, a current velocity of 1 m/s, and a wind velocity of 5 m/s) and as 164 hours in a shallow lake (the estimate assumes that the lake has a depth of 1 m, a current velocity of 0.05 m/s, and a wind velocity of 0.5 m/s). These estimates are in good agreement with those from Hamelink *et al.* (1996).

Within the TGD method (and EUSES) the volatilisation from surface water is not considered at a local level (but it is included in the regional and continental models).

The rate constant for volatilisation from soil is estimated as 2 d^{-1} for agricultural soil and 4 d^{-1} for grassland using the methods outlined in the TGD. These rate constants correspond to volatilisation half-lives of 0.35 days and 0.17 days, respectively, which are taken into account in the subsequent PEC calculations.

3.2.8 Precipitation

Although D4 has a high volatility, it also has a high log K_{ow} and so has the potential to adsorb onto atmospheric aerosols. However, the available experimental and modelling data indicate that, in the atmosphere, D4 is present almost entirely in the vapour phase (see Section 0). This, coupled with the low water solubility of D4, indicates that removal from the atmosphere by wet and dry deposition is likely to be minimal.

3.2.9 Bioaccumulation and metabolism

Several studies that investigated the accumulation and metabolism of D4 are available. ^{14}C-D4 was used in some of the accumulation studies. In these experiments measurements of body burdens (and hence accumulation factors) based on total ^{14}C measurements may overestimate the actual accumulation of D4 (as such measurements may include contributions from metabolites) when compared to measurements based on parent-compound analysis. In the Section 3.2.9.1, care is taken to distinguish clearly the actual basis for the measurements.

3.2.9.1 Experimental data

Fackler *et al*. (1995) studied the bioconcentration of ^{14}C-D4 in fathead minnows (*Pimephales promelas*) in a flow-through system with no headspace. The test system was designed to prevent loss of D4 from the water phase by volatilisation. Two studies were carried out and the purity of D4 was >98 per cent.

The first test was a preliminary study in which a six day exposure period was followed by a 14 day depuration period. The second, definitive, study used a 28 day exposure period followed by a 14 day depuration period.

The fish used were all ≤6 months old and had a mean weight of 0.48 g and a lipid content of 6.4 per cent. The water used in the test was soft (hardness 32–34 mg/l as $CaCO_3$) well water with a pH of 6.9–7.2 and a dissolved oxygen concentration of 72–87 per cent of saturation. The flow rate provided 8.1–9.2 tank volume replacements each day, and the test was carried out at 21–22°C.

D4 was added to the inflowing dilution water as a solution in acetone to give a nominal exposure concentration of 0.5 µg/l. The final amount of acetone in the dilution water was 3.3 µl/l (a similar amount of acetone was also added to the control solution). The test system was tested for several weeks prior to the addition of the fish [30 per vessel in the preliminary study and 70 per vessel in the definitive study, with two treatments (one for the BCF determination and one for metabolite determination) and one control vessel]. The initial biomass loading in the definitive study was 0.07 g/l. Water samples (triplicate samples) were analysed for ^{14}C-residues two days prior to the addition of the fish, daily during the exposure period, and on days one, three, seven, ten, 12, and 14 of the depuration period. Fish were sampled for whole-body ^{14}C-residues on days one, two, three, four, five, and six of exposure in the preliminary study, days one, three, seven, ten, 14, 18, 22, and 28 of exposure in the definitive study, and on days one, three, seven 12, and 14 of the depuration phase.

In the preliminary study, the mean measured concentration of ^{14}C-D4 in water was 0.51 µg/l and 0.41 µg/l in the two exposure vessels. The BCFs determined were found to increase with time, but there was no statistical difference between the values obtained on days three, four, and five. The mean BCF for this period was 3800 l/kg based on total ^{14}C measurements. The BCFs after six days of exposure were 4300–7000 l/kg and 4900–5400 l/kg in the two replicates, again based on total ^{14}C measurements. The uptake and depuration rate constants derived are 870 d^{-1} and 0.12 d^{-1}, respectively (a second model used gave the uptake rate constant as 1200 d^{-1}). Using these data the steady state BCF is estimated as around 7400–10,000 l/kg based on total ^{14}C measurements and the time to 90 per cent of steady state is estimated as 19 days.

The mean measured exposure concentration in the definitive study was 0.23 µg/l. Steady state was reached on day seven of the study and the mean steady-state fish concentration was 2826 µg/kg whole body. This gives a steady-state BCF of 12,400 l/kg based on total ^{14}C measurements. The 95 per cent confidence interval for the BCF is 9830–16,100 l/kg. The uptake and depuration rate constants derived in the definitive study are 2450 d^{-1} and 0.183 d^{-1}, respectively, to give an estimated steady-state BCF of 13,400 l/kg based on total ^{14}C measurements, which is in very good agreement with the value determined directly.

The tissues of fish on day 28 of the exposure were analysed in more detail. Around 92.7 per cent of the ^{14}C in the fish was extractable with ethyl acetate, and was identified as D4. The non-extractable ^{14}C was distributed in the viscera (4.7 per cent) and carcass (2.6 per cent). These data show that the majority of ^{14}C taken up into the fish was as D4 rather than as metabolites, but implies that the BCF based on parent compound may be slightly lower than that based on total ^{14}C measurements. However, the concentration in water was also based on total ^{14}C measurements, which may overestimate the concentration of parent compound

in the water phase if excreted metabolites are present in the water (no information is available on the fraction of the radioactivity in the water phase that was parent compound). Thus, taking into account that 92.7 per cent of the radioactivity in the fish was parent compound, it is estimated that the BCF based on parent compound alone is ≥11,495 l/kg based on the steady-state data and ≥12,422 l/kg based on the kinetic data.

Annelin and Frye (1989) also studied the uptake of D4 from water by fish. The D4 used in this test was not radiolabelled and from a commercial source (no other information is given on the purity of the D4 used). The study used a resaturation method (whereby the exposure solution was continuously passed through a column that contains sand coated with D4) to maintain a reasonably constant exposure concentration. The bioconcentration experiments were carried out with fathead minnows (*P. promelas*) of approximately 0.5–2.0 g in size.

The water used in the test had a hardness of 104 mg/l as $CaCO_3$, a pH of 7.6, and a dissolved oxygen concentration of 8.0 mg/l. The exposure tank had a total volume of 120 l and the recirculation rate through the resaturation column was 10 l/hour. Exposure was for 14 days at 20°C. Both the water phase and the fish were analysed for D4 using a gas–liquid chromatography method. After 14 days of exposure, the concentration of D4 in the fish reached 150–200 mg/kg. The concentration of D4 in the water phase varied between 20 and 80 µg/l. Based on these data it is possible to estimate that the BCF for D4 is in the range 2500–10,000 l/kg based on parent-compound measurements.

The depuration of D4 from the fish is best described by a two-compartment pharmacokinetic model, with depuration half-lives of ~17 hours and ~120 hours for the two compartments, respectively. As well as D4, samples of water (and also faeces and aquarium wipe samples) were analysed for total 'dimethylsiloxane' content (to determine if any significant metabolites were present or building up in the recirculating system). These results are very similar to those obtained using D4-specific analysis, and indicate that no significant metabolism (or hydrolysis) of D4 occurs in the system.

Opperhuizen *et al.* (1987) studied the uptake and elimination of D4 through exposure via water or food in guppies (*Poecilia reticulata*) and goldfish (*Carassius auratus*). The exposures were to a mixture of cyclic siloxane oligomers (ranging from D3 to D9) and linear oligomers (ranging from hexamethyldisiloxane to hexadecylmethylheptasiloxane). The substances tested were from commercial sources not radiolabelled (no other information is available on the purity of the substances used). The analytical method involved analysis of the parent compound by gas chromatography equipped with a flame ionisation detector or a mass spectrometer. The spiked food was prepared by adding a solution of the test compounds in pentane to the food and evaporating the solvent. The concentrations in food that result are given as in the range 306–425 mg/kg for the cyclic oligomers in the goldfish experiments and 1008–1044 mg/kg in the guppy experiments, but when displayed graphically in the paper these concentrations appear to be around 1 mg/kg. No information is given on whether freshly spiked food was prepared at regular intervals during the experiment or how stable the concentrations were on storage of the food.

For the water-exposure experiments a saturated solution of the test substances was prepared using a continuous-flow saturation system. However, a film of test substance was always present on the surface of the water when solutions were prepared in this manner. The saturated solution was continuously circulated through the exposure vessels during the experiment. The actual concentrations in the test vessels are not reported. The water-exposure experiments were carried out with guppies only.

The guppies used in the test had an average weight and lipid content of 0.17 g and 6.5 per cent, respectively, and the goldfish of 1.8 g and 2.3 per cent, respectively. The tests were carried out at 22°C using a mixture of 50 per cent tap water and 50 per cent demineralised

water. The water was continuously aerated during the dietary exposure experiments and in the water-exposure experiments it was aerated with pure oxygen added via a capillary tube. In the feeding experiments the feeding rate used was 25 mg/g each day and the exposure period was for up to 12 weeks. In the water-exposure experiments the fish were exposed for 20 days. In all cases the exposed fish were placed on a clean diet and in clean water after the exposure period to monitor the depuration of the accumulated chemicals.

Uptake of the cyclic oligomers occurred in both the water-exposure experiments and the dietary exposure. For D4 the steady-state BCF was 1090 l/kg and the steady-state biomagnification factor (BMF) from the food experiment was 0.06 for guppies (similar results were given for goldfish). These values are based on parent-compound analysis. The depuration half-life was around 3.8 days. Given the uncertainties over the exposure concentrations discussed above, these values should be treated with caution.

Opperhuizen *et al*. (1987) also carried out a similar experiment in which the fish were exposed to either a single linear oligomer (hexadecylmethylheptasiloxane) or a single cyclic oligomer (D7). Some of these experiments provide evidence that cyclic siloxane products (ranging from D5 to D9) form in fish, but it cannot be established whether this was the result of impurities in the materials, or whether such materials were formed by transformation in the water phase followed by subsequent uptake or were formed by metabolic processes in the fish.

Bruggeman *et al.* (1984) attempted to determine the dietary uptake of D4 by guppies (*Po. reticulata*). The substance tested was not radiolabelled and from a commercial source (no other information on the purity of the substance tested is given). However, the experimental method used (the food was spiked by adding the D4 as a solution in toluene followed by evaporation of the solvent) meant that all of the D4 was lost from the food during sample preparation and so it was not possible to carry out the study for D4.

Dow Corning (2007) recently carried out a reliable fish feeding study using ^{14}C-D4 with a radiochemical purity of 99.1 per cent. The fish used in the test were rainbow trout (*O. mykiss*) with an average length of 52 mm (range 47–57 mm) and an average weight of 1.3 g (range 0.91–1.7 g) at the start of the test. The lipid content of the fish increased with time during the study, ranging from 3.44 per cent before the start of the test to 6.74 per cent at the end of the uptake phase to 7.85 per cent at the end of the depuration phase. The mean lipid content throughout the study was 5.83 per cent.

The food (trout chow, lipid content 14.8 per cent) was dosed directly with a nominal D4 concentration of 500 mg/kg and fed to the trout at a constant rate of 3 per cent wet body weight per day. The mean measured concentration of D4 in the food was 457 mg/kg (91 per cent of nominal; standard deviation ±19 mg/kg) based on measurements five days prior to the start of the test and on days 14, 22, 28, and 35 of the uptake phase of the test, and was stable throughout the duration of the test. A control group (receiving diet without D4) was also run. The study consisted of a 35 day uptake period followed by a 42 day depuration period.

The water used in the test was dechlorinated municipal water and had an average hardness of 132 mg/l as $CaCO_3$ and a pH of 7.0–7.7. A flow-through test system was used. Two replicate test chambers, each of which contained 70 fish at the start of the test, were used for each of the treatment group and the control group. The volume of water in each test chamber was 42 litres and the flow rates were adjusted to provide approximately ten volume additions per day. The temperature was maintained at 12°C ± 2°C and the dissolved oxygen concentration remained at >62 per cent of saturation throughout the test. No mortalities occurred during the study and all fish appeared normal and healthy throughout.

Fish tissues (three fish per sampling event) were analysed for the presence of both total ^{14}C and parent compound on days one, three, seven, ten, 14, 21, 28, and 35 of the uptake phase

and days one, two, four, seven, 14, 28, and 42 of the depuration phase. Prior to analysis, the digestive tracts of the fish were removed and analysed separately. In addition, when the fish reached a suitable size, the liver was also removed and analysed separately (carried out only during the depuration phase). Further fish were subject to whole-body autoradiography on days one, ten, and 35 of the uptake phase and days 2, 14, and 42 of the depuration phase. Water samples were collected daily during the uptake phase and on day one of the depuration phase and analysed for radioactivity.

The levels of D4 and total ^{14}C determined are summarised in Table 3.11. The concentrations in fish determined by parent-compound analysis were generally similar to those determined by total radioactivity analysis. This implies that most of the radioactivity present in the fish is as parent compound. Therefore it is expected that the results will be similar regardless of whether they are determined on parent compound analysis or total ^{14}C analysis.

Table 3.11 Uptake of ^{14}C-D4 by *Oncorhynchus mykiss* from food (Dow Corning, 2007)

Day	Mean concentration in fish minus digestive tract and liver[1] (mg/kg wet weight)[2]		Percentage of total radioactivity in digestive tract[3]	Concentration in fish including digestive tract and liver based on total radiolabel (mg/kg wet weight)[1]
	Parent compound	Total radiolabel		
Uptake phase				
1	3.61 ± 0.54	3.52± 0.49	59.6	9.29 ± 2.02
3	15.3 ± 1.4	14.6 ± 1.3	40.8	22.5 ± 2.2
7	26.9 ± 2.0	25.4 ± 1.9	27.2	32.8 ± 2.1
10	42.1 ± 2.3	40.2 ± 2.4	24.9	50.0 ± 3.0
14	47.5 ± 2.2	45.7 ± 2.0	26.0	57.5 ± 2.2
21	74.3 ± 2.5	71.1 ± 2.4	23.5	89.0 ± 3.7
28	87.2 ± 5.7	85.6 ± 5.5	20.1	98.3 ± 6.3
35	91.1 ± 7.4	89.8 ± 7.4	20.4	104 ± 8
Depuration phase				
1	100 ± 5.4	101± 5.4	18.9	112 ± 6
2	95.5 ± 4.6	95.5 ± 4.0	16.0	102 ± 4
4	83.0 ± 3.3	84.1 ± 3.4	18.4	91.9 ± 3.7
7	75.6 ± 6.7	71.5 ± 6.4	12.8	74.2 ± 6.9
14	54.5 ± 2.8	53.0 ± 2.8	15.1	57.3 ± 4.0
28	33.9 ± 2.7	32.9 ± 2.6	11.5	35.2 ± 2.6
42	18.6 ± 0.3	17.1 ± 0.3	12.9	19.0 ± 0.3

Notes:
[1]The concentration during the uptake phase includes the liver. The concentration during the depuration phase excludes the liver. The percentage of the total radioactivity in the liver was generally small (~0.5–0.8 per cent of the total).
[2]± = standard error.
[3]Figures represent the percentage of the total amount of radiolabel present in the fish (as mg/fish) associated with the digestive tract.

The levels of D4 in the fish tissues appear to approach steady state by day 21 of the uptake phase [the concentrations of parent compound were not statistically significantly different ($p > 0.05$[16]) on days 21, 28, and 35] and the mean concentration present in the fish over this

[16]In the report the significant differences were tested using analysis of variance at $p > 0.05$ after checking for normality and homogeneity of variance using Shapiro–Wilk's test and Bartlett's test. It is

period was 84.2 mg/kg wet weight based on parent compound analysis (and 82.2 mg/kg wet weight based on ^{14}C analysis). Therefore the BMF based on parent compound is estimated as 0.18 on a wet weight fish/wet weight food basis. Taking into account the mean lipid content of the fish and the lipid content of the food, the lipid normalised BMF is estimated as 0.47 based on parent compound.

The uptake and depuration kinetics were also determined in the study. The rate constants for fish growth were determined during both the uptake phase (0.0389/day) and the depuration phase (0.0283/day). The growth-corrected uptake and depuration rate constants were 0.0119/day and 0.00659/day, respectively based on parent-compound analysis. The kinetic BMF is estimated as 1.8 on a wet weight fish/wet weight food basis using these growth-corrected rate constants. The growth-corrected depuration half-life is estimated as 105 days.[17]

Domoradzki (2008) indicates that the above rate constants for fish growth may be in error. These growth rate constants are estimated by linear regression using a natural log transformation of fish weight versus time (the exact method used is not totally clear). However, Domoradzki (2008) suggests that it is more appropriate to estimate the fish growth constant using the fish growth model:

$$\text{fish weight} = \text{initial fish weight} \times (1 + G \times \text{time}) \quad (3.2)$$

where G is the fish growth-rate constant (with units of time^{-1}).

Using this method to determine the growth rate constant, Domoradzki (2008) estimated a lower kinetic BMF of 0.62 on a wet weight fish/wet weight food basis for D4.

However, this approach to estimate the growth-corrected uptake and depuration appears to be in error as it is not the fish growth-rate constant itself that is important, but the rate constant for growth dilution, and these are not necessarily the same parameter. One way to estimate the growth dilution rate constant is to visualise a hypothetical fish in which the only process that reduces the concentration is growth dilution. For such a fish and assuming growth dilution is a first-order kinetic process (a fundamental assumption in the whole growth-correction procedure) the model is:

$$\frac{d[Concentration]}{dt} = -k_{growth\_dilution}[Concentration] \quad (3.3)$$

This can be solved to give:

$$\ln[\text{concentration}] = -k_{\text{growth dilution}} \times t + \text{constant} \quad (3.4)$$

Assuming that the initial amount of chemical in the fish is 1 mg (the amount assumed is not important for this analysis) then the concentration in the fish at any time (t) is estimated as [concentration] = 1/fish weight. Substituting this in Equation (3.4) shows that a plot of ln (1/fish weight) against time should lead to a straight line with a slope equal to $-k_{\text{growth dilution}}$. Such plots constructed using the raw fish weight data given in the Dow Corning (2007) report gave good straight lines. Furthermore, the values for the $k_{\text{growth dilution}}$ are almost identical to those used for the growth-rate constants in the original Dow Corning (2007) report. Therefore the correction proposed by Domoradzki (2008) does not appear to be appropriate and so is not considered further here.

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assumed here that this implies a >95% probability that the data were randomly sampled from the same population, although this is more usually expressed as $p < 0.05$. The alternative interpretation is that there was a >5% probability that the data were randomly sampled from the same population, which implies that steady state may not have been reached.

[17]The depuration half-life not corrected for growth is around 20 days. This shows the importance of fish growth as a depuration mechanism in this study.

The kinetic BMF on a lipid normalised basis was not reported in the Dow Corning (2007) study. Using the known lipid contents of the fish (mean 5.83 per cent) and food (14.8 per cent), the lipid normalised kinetic BMF can be estimated as around 4.6 based on parent compound.

The whole-body autoradiography showed that a significant amount of radioactivity remained in the gall bladder, with moderate amounts remaining in the gastrointestinal tract, liver, and gastrointestinal tract, at day 42 of the depuration phase. Smaller amounts of radioactivity remained in the other tissues and organs.

The concentration of total radioactivity present in the water samples was in the general range 0.4–1.7 µg/l during the uptake phase of the test (mean concentration around 0.9 µg/l). No parent-compound analysis was carried out on the water samples and so it is not clear if these concentrations relate to metabolites or to D4 itself. If the levels found do represent D4 it is possible that accumulation of D4 from the water phase could also occur.[18] However, it is likely that if D4 is present in the water phase it will be associated with faecal pellets and other particulate matter and hence may not necessarily be available to bioconcentrate in the fish.

The above-quoted concentrations, kinetics, and BMFs are based on the concentration of parent compound in fish tissues minus the contribution from the digestive tract. The amount of radioactivity in the digestive tract was determined separately in the study and these results, expressed as the percentage of the total radioactivity per fish, are summarised in Table 3.11. As can be seen, the amount of radioactivity in the digestive tract makes a significant contribution to the total amount of radioactivity in the fish, particularly during the uptake phase, but also during the depuration phase, during which it contributes around 13–19 per cent of the total amount. The test report indicates that 'the observation that the concentration of radioactivity/parent D4 remained high in the digestive tract even after dosing was discontinued is suggestive of parent D4 re-entering the digestive tract and subsequent elimination via the digestive tract'.

The results from analysis of the liver samples collected during the depuration phase suggest that some metabolism of D4 occurs. The concentration of parent compound in the liver samples is generally lower than the concentration of total ^{14}C in the liver (the percentage of the total ^{14}C in these samples attributable to parent compound is in the range 49–77 per cent, and the percentage decreases as the depuration time increases). In addition, liver extracts were analysed for metabolites using high performance liquid chromatography with radiochemical detection. These analyses confirmed at least one metabolite of D4 was present. It was not possible to establish the identity of this metabolite but, by comparison of the elution time with that of D4, it is thought that the metabolite is slightly less polar than D4.

Kent *et al*. (1994) investigated the accumulation of D4 by midge (*C. tentans*) larvae as part of a 14-day toxicity study. A commercial sample of D4 (purity 99 per cent) mixed with ^{14}C-D4 was tested. Three different sediments were used in the study, with organic carbon contents of 0.27, 2.3, and 4.1 per cent.. At the end of the 14-day exposure period, the midge larvae were analysed for total ^{14}C residues. The results of this analysis are summarised in Table 3.12. The levels in the midge are generally very similar to the levels in the sediment.

Table 3.12 Uptake of 14C-D4 by Chironomus tentans from sediment

Sediment	Mean	Sediment

[18]Given that the BCF for D4 is 12,400 l/kg, exposure to a concentration of D4 in water of 0.9 µg/l could theoretically lead to a body burden in the fish of around 11 mg/kg wet weight. This is around 13% of the total body burden found in this study at steady state.

Organic carbon content (%)	Mean concentration of ^{14}C-D4 (mg/kg dry weight)	concentration of ^{14}C-D4 in midge (mg/kg)	accumulation factor (based on total ^{14}C)
0.27	6.8	18	2.6
	17	30	1.7
2.3	18	22	1.3
	38	47	1.3
4.1	2.6	2	0.8
	7.4	5	0.7
	19	13	0.7
	54	34	0.6

The available accumulation data for D4 are summarised in Table 3.13. Overall the steady-state BCF of D4 in fish is 12,400 l/kg based on total ^{14}C measurements (92.7 per cent of the total ^{14}C in this experiment was present as parent compound). Other (less reliable) studies are available that support this value. Uptake of D4 by fish from food has also been investigated, but the feeding studies are not sufficiently consistent to determine a reliable accumulation factor. D4 can also be taken up by invertebrates from sediment. The factors found are in the range 0.6–2.6 (based on total ^{14}C measurements and on a dry weight in sediment concentration) and the actual sediment accumulation factor depends to some extent on the organic carbon content of the sediment.

For D4 it is also relevant to consider its uptake and metabolism in mammalian systems, particularly in relation to the secondary poisoning assessment. CES (2005a) summarises the available mammalian uptake and metabolism data for D4 [including a number of unpublished studies and taking into account published work by Varaprath *et al*. (1999, 2003), Plotzke *et al*. (2000), Andersen *et al*. (2001), and Sarangapani *et al.* (2003) on both D4 and D5]. Most of the available mammalian toxicokinetic and toxicity data were obtained using inhalation exposure (as this is one of the primary routes of exposure of humans and, given the volatility of D4, it is significantly easier to test the substance by this route of exposure than by dermal and oral routes), but dermal and oral exposure have also been considered. The behaviour of both D4 and D5 is broadly similar. It is concluded that the kinetics of D4 in rats after oral exposure are different to those after inhalation and dermal exposure. The kinetics of ^{14}C-D4 after inhalation and dermal exposure are very similar. Inhalation studies show that around 5 per cent of an inhaled dose is absorbed with higher levels in lung tissues and in fat than in other tissues. Elimination of the absorbed dose is rapid, and the primary routes of excretion are via water-soluble metabolites in urine (30–47 per cent of the dose), followed by exhaled air (30–35 per cent of the dose), and faeces (8–30 per cent). D4 also rapidly absorbs when administered as an oral dose in corn oil, either in simethicone or as a neat substance. The absorption is around 52 per cent of the dose in corn oil, around 12 per cent of the dose in simethicone, and 28 per cent of the dose as a neat substance.

Table 3.13 Summary of available bioaccumulation data for D4

Species	Exposure concentration	Value	Validity	Reference
Carassius auratus	306-–25 mg/kg food (mixture of oligomers)	Value not given, but reported to be similar to that for Po. reticulata (BMF ~0.06)	Invalid – exposure concentration not well-defined – based on parent compound	Opperhuizen et al. (1987)
	Saturated solution	Value not given, but reported to be similar to		

		that for Po. reticulata (BCF ~1090)		
Chironomus tentans	2.6–54 mg/kg dry weight in sediment	Sediment accumulation factors 0.6–2.6	Use with care – no information is given as to whether steady state was reached – not clear if based on total ^{14}C or parent compound (most likely total ^{14}C)	Kent et al. (1994)
Pimephales promelas	0.41–0.51 µg/l	BCF = 4300–7000 l/kg	Use with care – relatively short (six days) exposure period – based on total ^{14}C	Fackler *et al.* (1995)
	0.23 µg/l	BCF = 12,400 l/kg	Valid – steady state-value based on total ^{14}C – the estimated value based on parent compound is ≥11,495 l/kg	Fackler *et al.* (1995)
	20-80 µg/l	BCF = 2500–10,000 l/kg	Use with care – exposure concentration varied during the test and was close to (and in some cases above) the water solubility of D4 – based on total ^{14}C	Annelin and Frye (1989)
Poecilia reticulata	1008–1044 mg/kg food (mixture of oligomers)	BMF = 0.06	Invalid – exposure concentration not well-defined – based on parent compound	Opperhuizen *et al.* (1987)
	Saturated solution	BCF = 1090 l/kg		
	Dietary study		Invalid – exposure concentration not well-defined – based on parent compound	Bruggeman *et al.* (1984)
Oncorhynchus mykiss	457 mg/kg food	BMF = 0.18	Valid – steady-state value on a wet weight fish/wet weight food basis – based on parent compound	Dow Corning (2007)

		BMF = 0.47	Valid – steady-state value on a lipid-normalised basis – based on parent compound	
		BMF = 1.8	Valid – kinetic, growth-corrected value on a wet weight fish/wet weight food basis – based on parent compound	
		BMF = 4.6	Valid – kinetic, growth-corrected value on a lipid-normalised basis – based on parent compound	

Anderson (2005) and Reddy *et al*. (2004, 2005) also carried out physiologically based pharmacokinetic modelling for both inhalation and dermal exposure to D5 and D4 (CES, 2005a). These models are based on a comprehensive data set that included both single and repeated inhalation studies in rats, a single-inhalation exposure study in humans, and both *in vitro* and *in vivo* percutaneous absorption studies. The model includes a sequestered pool of D4 (presumed to be in lipoproteins) released from the liver, distributed by the blood, and cleared from the blood into fat. The inhalation model shows that metabolism and exhalation are important mechanisms by which D4 and D5 are eliminated, and that the rapid clearance via these two routes means that D4 does not accumulate, despite a high predicted blood-to-fat partitioning behaviour.

The dermal absorption model for D4 suggests very limited absorption, with only around 0.3 per cent absorbed systemically. Furthermore, the dermally absorbed dose is predicted to enter the venous circulation and move directly to the lungs where ~80 per cent is eliminated via exhalation prior to it being available systemically.

After oral exposure, D4 is thought to enter the blood via the lymphatics within the core of chylomicrons and other lipoproteins [and so is in a different form to that for inhalation or dermal routes of exposure (CES, 2005a)]. Therefore an assumption of rapid elimination via the lungs from an oral dose cannot be made. However, it is likely that the substance is rapidly metabolised and exhaled in mammals after oral exposure (in a similar way to the absorbed dose after inhalation exposure).

CES (2005b) reports a further (unpublished) review (Andersen, 2005) of the pharmacokinetics of cyclic siloxanes. Around 50 per cent of a dose of D4 administered orally by gavage in corn oil was systemically absorbed. This review concludes that oral dosing leads to more complex pharmacokinetics than inhalation or dermal dosing as the oral uptake appears to be associated with siloxanes as microemulsions. These microemulsions are not thought to dissolve readily in plasma and blood, and will be removed from the circulation initially by actions of cells of the reticuloendothelial system in liver (where the D4 is readily metabolised) and spleen. It also concludes that uptake after oral dosing may be associated with lipid transport, such as chylomicron formation, and so may not be available for metabolism or excretion via exhalation. Overall, the differences between oral dosing and inhalation and/or dermal dosing suggest a much higher persistence of D4 in blood after oral dosing, but that it is likely that this persistence is because D4 is in a pool within the body is

not as available. Thus, the results from oral studies that use relatively high doses in an oil vehicle should be used with caution when conclusions are drawn for more normal routes of exposure at lower doses.

Based on the above there is clearly some uncertainty in extrapolating the results from laboratory oral gavage studies, in which relatively high doses of D4 dissolved in a vehicle are used, to the situation in the environment where D4 is distributed in the body (probably associated with the lipid fraction) of the food organism (e.g. a fish). These different modes of administration could mean that for gavage studies D4 is in a different form within the gut to that from feeding in the wild.

Overall it is concluded that D4 is likely to be rapidly eliminated from mammalian systems and so appears to have a low potential to accumulate in mammals. However, pharmacokinetic behaviour after oral administration is complex, and is not as well understood as other routes of exposure.

3.2.9.2 Calculated BCFs and BMFs

BCF values for fish and earthworms can be estimated from log K_{ow} values using the methods outlined in the TGD (the equivalent values using a log K_{ow} of 5.1 are also given):

- for log K_{ow} 6.49 the BCF for fish is 43,500 l/kg and that for earthworms is 37,100 l/kg;
- for log K_{ow} 5.1 the BCF for fish is 4320 l/kg and that for earthworms is 1510 l/kg.

The predicted value for fish is much lower than that found experimentally, and so the experimentally determined values are used in this assessment. No experimental value is available to compare with the predicted BCF for earthworms.

Using the experimentally determined BCF for fish of 12,400 l/kg based on total ^{14}C measurements, the default BMFs from the TGD appropriate for the secondary poisoning assessment of D4 are:

- a BMF1 for predators of 10
- a BMF2 for top predators of 10.

Some feeding studies carried out with fish exposed to D4 via the diet show only a low level of uptake, which implies that a BMF lower than the default value of ten is appropriate for D4, but these studies are of generally low reliability. A more recent reliable feeding study with fish (Dow Corning, 2007) gives, based on parent compound, BMFs for D4 of:

- 0.18, steady-state value on a wet weight fish/wet weight food basis;
- 0.47, steady-state value on a lipid-normalised basis;
- 1.8, kinetic, growth-corrected value on a wet weight fish/wet weight food basis;
- 4.6, kinetic, growth-corrected value on a lipid-normalised basis.

These values are considered the best-available data on the actual BMF of D4 and so are used in this assessment in preference to the TGD default values. The key question for the assessment is therefore which of these values is most appropriate to use in the PEC calculations.

The TGD recommends that the BMF value used should, where possible, be lipid normalised and so the lipid-normalised values from above appear to be most appropriate for this risk assessment. The TGD does not give any guidance as to whether growth-corrected BMFs should be used in preference to BMFs that are not growth corrected. For D4 this is an important consideration as the depuration seen in the Dow Corning (2007) study is dominated by growth dilution, which has implications for the accumulation likely to occur in slow-growing adult fish compared with that in fast-growing juvenile fish. Thus, although the steady-state lipid-corrected BMF is 0.47 in this study, it is possible that much higher levels of accumulation could occur in adult fish and so it is considered relevant to use the growth-corrected and lipid-normalised BMF of 4.6. This value is therefore used for the BMFs of both predators and top predators in this assessment. Although this value is corrected for both lipid content and growth of the fish, there are further difficulties in extrapolating the results of laboratory feeding studies to the field situation as one of the key determinants is the assimilation or absorption efficiency of the chemical in the gut. This depends on, among other things, the digestibility of the food consumed and it is possible that the digestibility of

the food used in laboratory studies (trout chow in this case) may not represent the digestibility of prey in the natural aquatic environment.

Based on the available toxicokinetic information D4 appears to have a relatively low potential for accumulation in mammals (certainly lower than might be expected based on the high log K_{ow} and the high fish BCF values). However, the BMFs here are used to estimate the concentration that results in food (e.g. fish) for consumption by mammalian and avian predators and not that in the mammalian and avian predators. Thus it is biomagnification in fish that is the most important consideration here. Therefore, although the bioaccumulation potential of D4 in mammals appears to be relatively low, for the secondary poisoning assessment this cannot be used alone to show a low bioaccumulation potential in the food chain.

3.2.9.3 Summary of bioaccumulation

The available experimental data show that D4 bioconcentrates in fish. The highest value for the steady-state BCF is 12,400 l/kg based on total ^{14}C measurements and this value is used in the assessment. Although this value may contain a contribution from both metabolites and parent D4, parent-compound analysis indicates that a large proportion of the body burden (~93 per cent) is parent compound. Therefore it is considered appropriate to use this value in the risk assessment as a realistic worst-case approach. Uptake into aquatic organism from food is also likely to occur and a realistic worst-case BMF for D4 is thought to be around 4.6 on a growth-corrected and lipid-normalised basis.

In summary, the accumulation factors used in this assessment are:

- BCF for fish, 12,400 l/kg
- BMF1 for predators, 4.6
- BMF2 for top predators, 4.6
- BCF for earthworms , 37,100 l/kg.

3.3 Environmental concentrations

In this section we outline the predicted and available measured concentrations in various environmental compartments. The predicted concentrations are estimated using EUSES 2.0.3, which implements the methods outlined in the TGD.

The wide uses of silicone compounds in general (some of which may contain trace amounts of D4) and the use of D4 itself in personal care products mean environmental samples can be contaminated during storage and handling in the laboratory and so measured concentrations may not reflect the actual environmental conditions. For example, Helmig *et al.* (1989) found D4 (and other cyclic oligomeric siloxanes) in laboratory blank samples from various adsorption tubes used to collect air samples. The compounds are thought to originate from the column coating or the sealing material in the gas chromatographic system used. Similarly, Gasking (1988) reports that the breakdown of septa used in gas chromatography could be a source of silicone oligomers. Furthermore, Varaprath *et al*. (2000) conclude that PDMS-based gas chromatography stationary phases could generate D4 through reaction with water present in extracts if they are not thoroughly dried prior to injection onto the column; similar effects are reported by Knobloch and Engewald (1995). In a recent poster presentation, Varaprath *et al.* (2005) highlighted the analytical problems that

may be encountered when silicones are analysed. Therefore, to validate measured data for use in risk assessment, it is vital that the responses in the laboratory blank samples (and other relevant quality-assurance details) are reported in the original paper to avoid 'false positive' results.

Also relevant is that D4 is a highly volatile substance, particularly from water, and therefore to avoid potential loss from volatilisation care is required during sample collection, storage, and, in particular, extraction procedures. The results from recovery experiments are a useful insurance in this respect.

3.3.1 Aquatic compartment (surface water, sediment, and wastewater treatment plant)

3.3.1.1 Predicted environmental concentrations

The predicted concentrations in surface water, sediment, and wastewater are summarised in Table 3.14.

Table 3.14 Predicted concentrations in surface water, sediment, and wastewater treatment plants

Scenario	PEC		
	Surface water (µg/l)	**Sediment (mg/kg wet weight)**	**Wastewater treatment plant (mg/l)**
Production and on-site use as an intermediate – UK site	3.9	1.5	0.010
Off-site use as an intermediate – polymers – wet process – UK sites	7.5×10^{-3}	2.8×10^{-3}	3.6×10^{-4}
Off-site use as an intermediate – polymers – wet process – EU sites	2.4×10^{-3}	8.8×10^{-4}	1.2×10^{-9}
Off-site use as an intermediate – polymers – dry process – UK sites	2.4×10^{-3}	8.8×10^{-4}	0
Off-site use as an intermediate – polymers – dry process – EU sites	2.4×10^{-3}	8.8×10^{-4}	0
Off-site use as an intermediate – silica treatment – UK and EU sites	2.4×10^{-3}	8.8×10^{-4}	0
Personal care products – formulation – UK sites	2.5×10^{-3}	9.2×10^{-4}	1.1×10^{-6}
	2.7×10^{-3}	1.0×10^{-3}	3.4×10^{-6}
	2.5×10^{-3}	9.1×10^{-4}	7.7×10^{-7}
	2.5×10^{-3}	9.2×10^{-4}	1.0×10^{-6}
	2.8×10^{-3}	1.0×10^{-3}	4.3×10^{-6}
	3.1×10^{-3}	1.2×10^{-3}	7.5×10^{-6}
	3.9×10^{-3}	1.5×10^{-3}	1.6×10^{-5}

Scenario	PEC		
	Surface water (µg/l)	Sediment (mg/kg wet weight)	Wastewater treatment plant (mg/l)
	2.9×10^{-3}	1.1×10^{-3}	5.0×10^{-6}
	2.8×10^{-3}	1.0×10^{-3}	4.1×10^{-6}
	2.8×10^{-3}	1.0×10^{-3}	4.2×10^{-6}
	2.8×10^{-3}	1.1×10^{-3}	4.7×10^{-6}
	2.7×10^{-3}	1.0×10^{-3}	3.8×10^{-6}
Personal care products – formulation – generic site (non-UK)	0.018	6.7×10^{-3}	1.6×10^{-4}
Personal care products – use by general public	9.0×10^{-3}	3.3×10^{-3}	6.8×10^{-5}
Household products – formulation	7.6×10^{-3}	2.8×10^{-3}	5.4×10^{-5}
Household products – use	3.0×10^{-3}	1.1×10^{-3}	6.1×10^{-6}
Regional	2.4×10^{-3}	1.7×10^{-3}	

3.3.1.2 Measured environmental concentrations

Boehmer and Gerhards (2003) studied levels of D4 in various water systems in Europe. Precautions were taken during the sample collection (i.e. aeration and bubbling of the sample were avoided and sealed containers with no headspace used for storage) and analysis to avoid loss through volatilisation. The analytical method used had a detection limit of 0.02 µg/l. Laboratory blank samples were run at regular intervals. On occasions, traces of D4 were found in the blank samples. In these cases the average blank value was subtracted from the field values, and the detection limit then set as twice the average blank value. The recovery of the method is in the range 90–140 per cent for D4 concentrations of 1–2 µg/l, which is considered acceptable given the low concentrations.

The levels of D4 found in industrial WWTPs at silicone production sites and municipal WWTPs are summarised in Tables 3.15 and 3.16, respectively. The concentrations in influent refer to total concentrations (i.e. adsorbed plus dissolved).

Table 3.15 Concentration of D4 in silicone industry wastewater treatment plants in Europe (Boehmer and Gerhards, 2003)

Location of silicone producer	Sampling data	D4 concentration (µg/l)			Estimated removal in treatment plant (%)
		Influent	Effluent	Downstream	
Germany I	January 2001	1090, 972	16.4 and 15.0	<0.02	98.5
Germany II	7 February 2001		9.3	<0.02	
	8 February 2001		0.5	<0.02	
	9 February 2001		1.2	<0.02	
France	March 2001	6400, 2941, 2828	0.65 1	<0.02 1	>99.9 1
UK			2.9 and 5.2	1.0 and 1.2	

Note: [1]The effluent and downstream samples may have been taken at different times to the influent samples.

Table 3.16 Concentration of D4 in municipal wastewater treatment plants in Europe (Boehmer and Gerhards, 2003)

Wastewater treatment plant	Sampling data	D4 concentration			Estimated removal in treatment plant (%)
		Influent (µg/l)	Effluent (µg/l)	Sewage sludge (mg/kg dry weight)	
Meltenham – UK	September 2000	2.2	0.31	No data	86
Crofton – UK	September 2000	3.8	0.16	No data	96
WWTP 1 – Germany	Spring 2000	4.2	<0.1	0.13	>98
WWTP 2 – Germany	Spring 2000	0.7	<0.1	0.07	>86
WWTP 3 – Germany	Summer 2000	0.23, 0.33, 0.48	No data	0.01	

IUCLID (2005) reports the levels of D4 in WWTP influent and effluent at a plant in Germany (Martin *et al*., 1996). The levels found were 1.7 µg/l in influent, 2.3 µg/l in primary sludge (1.2 per cent total solids content), 5.3 µg/l in secondary sludge (0.95 per cent total solids content), and 0.5 µg/l in effluent.

Aramendía *et al*. (1998) detected D4 at concentrations of 0.10 µg/l and 0.021 µg/l in two samples of effluent from a WWTP in Córdoba, Spain. The first sample was collected when

the plant was working poorly (as a result of a failure in the biological treatment system) and the second was collected when the plant was operating correctly. No quality-assurance details are reported.

The levels of D4 in marine water samples taken from the mouth of the River Mersey (six samples collected in January 2001) and Cardiff Bay (six samples collected in February 2001) are all below the limit of detection [0.02 µg/l for the River Mersey samples and 0.04 µg/l for the Cardiff Bay samples (Boehmer and Gerhards, 2003)].

Bruggeman *et al.* (1984) report the results of an earlier study [de Groot (1979), in Dutch] that found traces of D4 in water from the River Rhine in 1979.

Boehmer and Gerhards (2003) also determined the levels of D4 in river sediments and marine sediments from Europe. The results of these analyses are summarised in Table 3.17.

Table 3.17 Concentration of D4 in sediments in Europe (Boehmer and Gerhards, 2003)

Location	Measured concentration (µg/kg dry weight)[1]	Comment
	Freshwater	
River Rhine	Not detected	Sampled at Karlsruhe
	<3	Sampled at Wiesbaden
	Not detected	Sampled at Koblenz
	Not detected	Sampled at Köln
	Not detected	Sampled at Leverkusen
	12	Sampled at Krefeld
	Not detected	Sampled at Emmerich
	Not detected	Sampled at Hollands Diep
Hall Dike Creek	5, 6, 7	3.5 km downstream of a WWTP
	Marine	
River Mersey (mouth)	<3 (in all six samples)	Six samples collected January 2001
Cardiff Bay	28, 28, 47, 45, 15, 32	Six samples collected February 2001
Coast of Scotland (LAS St. Abbs)	Not detected	Site previously used for sewage sludge disposal; three samples collected in July 2000
Coast of Scotland (Bell Rock)	Not detected	Site previously used for sewage sludge disposal; six samples collected

Note: [1]The limit of detection was set at 1 µg/kg dry weight. The limit of quantification (LOQ) was set at three times this limit (i.e. 3 µg/kg dry weight).

Boxall and Maltby (1995) tentatively identified D4 in a sample of stream sediment (top 2 cm) taken from close to an outfall for road run-off from the M1 motorway in the UK. No details of the level present or quality-assurance details are given.

A survey of influent, effluent, and removal efficiency of D4 was carried out in WWTPs in New Jersey and New York, USA (Kent *et al.,* 1994; Chandra, 1997). The mean influent

concentrations at five plants were in the range 0.64–7.09 µg/l and the mean effluent concentrations at the plants were 0.06–0.41 µg/l, with most being below 0.2 µg/l. The overall removal efficiency at the four treatment plants using activated sludge was 94–99 per cent. The overall removal efficiency at the oxidation ditch treatment plant was lower, at 62 per cent.

McFall *et al*. (1985) detected D4 in water samples from Lake Pontchartrain (a shallow oligohaline estuary), USA. The samples were collected at the Inner Harbour Navigation Canal at a depth of 1.5 m on the ebb tide in May 1980 and at depths of 1.5 m and 10 m on the flood tide in June 1980. D4 was not detected in the ebb-tide sample or in the 10 m depth flood-tide sample (the detection limit is not stated), but was found in the 1.5 m depth flood tide sample at a concentration of 0.03 µg/l. No information is reported on the laboratory blanks in this study and so the findings should be treated with caution.

Desideri *et al.* (1991) detected D4 in samples of seawater (ten samples) and pack ice (three samples) from Terra Nova Bay, Antarctica. The samples were collected in 1988–1989 and organic compounds extractable by n-hexane were screened for using gas chromatographic techniques. The concentration of D4 was 4–28 ng/l in nine of the ten seawater samples analysed and 20-81 ng/l in all three pack ice samples analysed. D4 was not detected in the seawater particulates or the pack-ice particulates. No quality-assurance data are reported, except that the quantification limit was twice the detection limit. In follow-up studies to identify non-chlorinated organic compounds (extractable by n-hexane) in Arctic snow and pack ice, no occurrence of D4 is reported (Desideri *et al.*, 1994, 1998).

Kent *et al*. (1994) and Hobson (1995) report the results of the analysis of 21 sediments from Chesapeake Bay. The study was a follow-up study to work by Pellenbarg (1985), who measured the total concentrations of organosilicon compounds in sediments from the area (upper reaches to the mouth of Chesapeake Bay). The samples were collected in 1985 from six rivers and harbours and D4 was found in only one (from Rouge River) at a concentration of 185 µg/kg dry weight. The detection limit of the method used was 132 µg/kg dry weight.

IUCLID (2005) reports a study in 1985 (unpublished) in which D4 was detected in one out of six sediment samples taken from three large freshwater harbours and river estuaries in the USA. The level detected was 0.07 mg/kg dry weight (the detection limit of the method was 0.05 mg/kg dry weight). Similarly, in the same study, D4 was not detected in five samples of sediment collected from three salt water estuaries in the USA.

IUCLID (2005) reports the results of Linders *et al*. (1981) and Morra *et al.* (1979), who found D4 in water from the River Rhine at concentrations of 0.03–0.3 µg/l (samples from 1978) and 0.03–0.1 µg/l (samples from 1979). No further details of these studies are available.

Kaj *et al.* (2005) recently surveyed the levels of D4 in water and sediment in Sweden. The samples were collected mainly during 2004. The sampling and analytical methods used were designed to avoid both loss of D4 from the sample through volatilisation and contamination of the sample by D4. The levels found are summarised in Table 3.18. The water and sediment samples were collected from sites both near to potential industrial point sources and in more remote areas, and include both freshwater and coastal sites. However, few details of the potential point sources are given, and it is not clear if D4 was actually used in these areas.

Overall, the levels in surface water and sediment found in this study appear to be generally low, but only relatively few surface water samples were included in, and these were generally taken from industrial areas in which it is unclear whether or not D4 was used at the time.

Table 3.18 Concentration of D4 in water and sediment from Sweden (Kaj et al., 2005)

Location	Measured concentration	Comment
Surface water (µg/l)		
Stenungsund	<0.06	Site near to potential point sources in an industrial area
Stenungsund	<0.06	Site near to potential point sources in an industrial area
Stenungsund	<0.06	Site near to potential point sources in an industrial area
Bay outside Stockvik	<0.06	Site near to potential point sources in an industrial area
Sediment (ug/kg dry weight)		
Ö Gotlandsdjupet	<22	Background site
Ö Öland	<44	Background site
Norrköpingsdjupet	<14	Background site
Stenungsund	<9	Site near to potential point sources in an industrial area
Stenungsund	<14	Site near to potential point sources in an industrial area
Stenungsund	<18	Site near to potential point sources in an industrial area
Bay outside Stockvik	<11	Site near to potential point sources in an industrial area
Bay outside Stockvik	<22	Site near to potential point sources in an industrial area
Bay outside Stockvik	<11	Site near to potential point sources in an industrial area
Bay outside Stockvik	<12	Site near to potential point sources in an industrial area
Lake Bäsingen	<19	
Lake Venjan	<47	
Gröpplebäcken	<16	
Hulingen	<44	
Verserum	<6.9	
Mouth of Emån	<12	
Ivösjön	<60	
Helsingborg	<16	
Hammarsjön	<20	
Storarydsdammen	<28	
Himmerfjärden	<23	
St Envättern	<115	
Lake Vänern, Åsfjorden	<28	
Lake Vänern, Kattfjorden	<23	
Skuten	<28	
Close to a pulp and paper	<16	

Location	Measured concentration	Comment
production plant Roxen	<45	
	Wastewater (ug/l)	
Influent to municipal WWTPs	<0.07	Not detected in any of four sewage treatment plants (detection limit 0.07 µg/l)
Effluent samples from municipal WWTPs	<0.07	Not detected in any of 12 samples (detection limit 0.07 µg/l).
Industrial effluent	<0.07	Effluent from a pulp and paper production plant
Industrial effluent	<0.06	Effluent from a factory (possibly a chemical plant but it is not clear what was being manufactured)
Well water from factory site	<0.06	Well water from a factory (possibly a chemical plant but it is not clear what was being manufactured).
Percolate waters from landfills	<0.07	Not detected in three samples

TemaNord (2005) recently measured of the levels of D4 in wastewater (influent and effluent), surface water, and sediment in Nordic countries (including Denmark, Faroe Islands, Finland, Iceland, Norway, and Sweden). The sampling and analytical methods used were designed to avoid both loss of D4 from the sample through volatilisation and contamination of the sample by D4. The samples were collected during 2004 and 2005. The results of the survey are summarised in Table 3.19.

Table 3.19 Concentration of D4 in water and sediment from Nordic countries (TemaNord, 2005)

Sampling location[1]		Concentration
		Water (µg/l)
Denmark	Coastal area, Kattegat	<0.04
	Coastal area, innerfjord, Roskilde	<0.04
	Coastal area, Øresund Lynetten, Kobenhavn	<0.04
	Kobenhavn, Lynetten STP influent	0.28
	Kobenhavn, Lynetten STP effluent	<0.06
	Roskilde, Bjergmarken STP influent	0.60
	Roskilde, Bjergmarken STP effluent	<0.06
	Avedöre landfill leachate	<0.08
	Uggelöse landfill leachate	<0.08
Faroe Islands	Torshavn, Sersjantvikin STP effluent	<0.08
	Torshavn, Húsarhaga landfill leachate	<0.08
Finland	Ämmässuo, landfill and waste tip leachate	<0.4
	Influent to Nokia City Kulloonvuori STP (tyre industry wastewater)	3.7

	Sampling location[1]	Concentration
	Influent to Nokia City Kulloonvuori STP (floor industry wastewater)	0.25
	Treated effluent, Kulloonvuori STP	<0.06
	Treated effluent, Kulloonvuori STP	0.11
	Espoo City Suomenoja STP effluent	<0.08
	Helsinki City Vilkinmäki STP effluent	<0.08
Iceland	Alfnes landfill runoff water	1.1
	Reykjavik, seawater	<0.05
	Reykjavik, seawater	<0.05
	Reykjavik, seawater	<0.05
	Reykjavik, seawater	<0.05
Norway	Arendal STP influent	<0.3
	Arendal STP effluent	<0.07
	Lake Bergsjøen (background area)	<0.06
	Lake Røgden (background area)	<0.09
	Outer Oslofjord (coastal background)	<0.07
	Inner Oslofjord (urban area)	<0.07
	Spillhaug landfill runoff water	<0.08
	Bölstad landfill runoff water	<0.07
	Grönmo landfill runoff water	<0.07
Sweden	River Nissan (upstream of storm water effluent)	<0.07
	River Nissan (storm water effluent)	<0.07
	River Nissan (downstream of storm water effluent)	<0.07
	Högbytorp landfill (untreated percolate water)	<0.12
	Högbytorp landfill (treated percolate water)	<0.09

		Sediment (µg/kg dry weight)
Denmark	Coastal area, Kattegat	<3
	Coastal area, Øresund, Lynetten	<5
	Coastal area, Roskilde	84
Faroe Islands	Kaldbakfjordur (influenced by pollution from unidentified sources)	<11
Finland	Helsinki, Vakal (Old City Bay – site influenced by historical pollution from a former hazardous waste combustion plant)	<20
	Espoo coastal sea area	<20
Iceland	Sediment 1	<4
	Sediment 2	<3
	Sediment 3	<10
	Sediment 4	<7
Norway	Lake Bergsjøen (background area)	<60
	Lake Bergsjøen (background area)	<65
	Lake Røgden (background area)	<50
	Lake Røgden (background area)	<50
	Leanbukta	<20
	Vrengansundet	<10
	Brödrene Sunde Verft	<11
Sweden	Gislaved, Nissan (storm water effluent)	<2
	Gislaved, Nissan (downstream of storm water effluent)	<2
	Gislaved, Nissan (upstream of storm water effluent)	<3

Sampling location[1]	Concentration
Stockholm, Essingen	<13
Stockholm, Riddarfjärden	<9
Ö Gotlandsdjupet	<30
Ö Landsortsdjupet	<30

Note: [1]STP, sewage treatment plant.

D4 was found in several influent samples (up to 3.7 µg/l) and one effluent sample (at 0.11 µg/l) from sewage treatment plants. In addition, D4 was detected in one marine sediment sample at a concentration of 84 µg/kg dry weight. The levels of D4 in surface water and other sediment samples were generally very low (not detectable).

Schlabach *et al*. (2007) followed up to the TemaNord (2005). They investigated the levels of D4 in influent and effluent from two sewage treatment plants that discharge to the Inner Oslofjord in Norway (Bekkelaget STP and VEAS STP), as well as the levels in water and sediment from the Inner Oslofjord itself. The sampling and analytical methods used were designed to avoid loss of D4 from the sample through volatilisation and contamination of the sample by D4. The samples were collected in September and October 2006. The results are summarised in Table 3.20.

Table 3.20 Concentration of D4 in water and sediment from the Inner Oslofjord (Schlabach et al., 2007)

Sampling location[1]	Concentration
	Water (µg/l)
Bekkelaget STP influent	0.1
Bekkelaget STP effluent	<0.03
VEAS STP influent	0.2
VEAS STP effluent	0.1
Seawater, Bekkelaget	<0.03
Seawater, Lysaker	<0.03
Seawater, Vestfjord/Nesodden	<0.03
Seawater, Færder	<0.03
	Sediment (µg/kg dry weight)
Bekkelagsbassenget	<4
Bekkelagsbassenget	<38
Lysaker	<33
Lysaker	<31
Vestfjord/Oslofj	<21
Vestfjord/Oslofj	<23

Note: [1]STP, sewage treatment plant.

D4 was in the influent to both sewage treatment plants, and in the effluent from one sewage treatment plant at very low concentrations, but it was not detectable in seawater or sediment. These findings are similar to those of the TemaNord (2005) survey.

Environment Canada (2008) reports the results of an unpublished survey of the levels of D4 in the influent and effluent of WWTPs in Canada. Nine WWTPs were surveyed. The plants were located in large urban centres in southwestern Ontario and the survey included

conventional secondary and tertiary water treatment plants and lagoons. The plants were sampled in October 2005 and in winter 2005. The concentrations of D4 were between <2 and 24 µg/l in the influent samples and between <2 and 2.9 µg/l in the effluent ones. Environment Canada (2008) indicates some evidence for higher influent concentrations in the winter samples (range 2.8–21 µg/l[19]) than in the samples taken in October (concentration generally <2 µg/l), but that the concentration in effluent was similar in both the October samples and the winter samples. No information on the number of samples analysed at each plant is given and no quality-assurance data are reported, and therefore the significance of the apparently higher influent concentrations in winter compared with autumn (October) is unclear.

Powell and Kozerski (2007) report the results of a monitoring study to investigate the levels of D4 in sediments and sediment cores from Lake Ontario. Surface sediment samples (upper 5 cm) were collected from five sites (Toronto Harbour, Kinston Basin, Rochester Basin, Mississauga Basin, and Niagara Basin), with sediment cores also collected at three of these sites (Rochester, Mississauga, and Niagara basins). D4 was detected at a concentration of 287 µg/kg dry weight (130 µg/kg wet weight) in surface sediment from Toronto harbour, but was not detected in surface sediments from the other (more remote) sites or sediment cores (no sediment core was taken from Toronto harbour). The method limit of detection was around 5.8 µg/kg dry weight for D4. The sample collection and analytical methodology used included comprehensive quality-assurance and quality-control procedures to prevent problems of contamination of the samples by D4 or loss of D4 during the analytical procedure.

Paxéus (2000) detected D4 at a concentration of 1–2 µg/l in leachate from three landfill sites (two active landfills and one in operation from 1938 to 1978) in Sweden. No quality-assurance data are reported.

3.3.1.3 Comparison of measured levels with predicted levels

Monitoring data are available for the levels of D4 in surface water downstream of the silicones production site in the UK. The measured levels downstream of the plant (around 1 µg/l) compare reasonably well with the predicted level of 3.9 µg/l.

Measured data are available for municipal WWTPs in Europe. These data could be compared with the scenarios that consider the use of D4 by the general public (in particular, use of personal care products and of household products). However, there has been a reduction in use of D4 in personal care products in recent years and so the older monitoring data may not reflect the current levels of D4. The available monitoring data from such plants indicate that the influent concentration of D4 was in the range 0.1–4 µg/l with similar levels in plants from the UK, Germany, and some Nordic countries. This compares with the predicted influent concentrations to the WWTP of around 1.9 µg/l for use of personal care products and 0.17 µg/l for use of household products. Therefore there is reasonable agreement between the predicted levels of D4 in these applications and those found in actual samples of wastewater effluent. Similarly, the measured effluent concentrations from such plants are in the range <0.1 to 0.13 µg/l, which again is in reasonable agreement with the effluent concentrations predicted for personal care products (around 0.07 µg/l) and household products (around 0.006 µg/l). The relatively small differences between the predicted and measured concentrations may result from lower amounts of D4 currently being used in this

[19]The range maximum concentration in winter is given as 21.42 µg/l, but the overall maximum is given as 24 µg/l. It is possible that the 21 µg/l value is an error and the maximum concentration in water was 24 µg/l.

application compared with the situation when the samples were taken (some studies relate to 2000).

For sediment, direct comparison between the predicted and measured concentrations is not possible as the levels predicted depend on the organic carbon content of the sediment and the conversion from wet weight to dry weight requires knowledge of the actual water contents of the sediments. D4 is in sediments at some locations in the UK and EU (e.g. concentrations of up to 0.012 mg/kg dry weight were measured in the River Rhine, up to 0.047 mg/kg dry weight in Cardiff Bay, and up to 0.084 mg/kg dry weight in the recent Nordic survey). Using the default water contents for sediment given in the TGD, concentrations of 0.012, 0.047, and 0.084 mg/kg dry weight are equivalent to concentrations of 0.003, 0.010, and 0.018 mg/kg on a wet weight basis. These are similar to those predicted for some scenarios, particularly those that relate to the use of D4 by the general public and to the regional scenario. However, it is not possible to make a more meaningful comparison directly with the scenarios considered in this assessment as the levels in the areas sampled may be influenced by a number of sources.

Much of the other monitoring data refer to countries other than those in the EU, or to older data, when the use pattern of D4 could be different to that in the UK and EU currently. Therefore no comparison is made between these data and the concentrations predicted in this assessment.

3.3.2 Terrestrial compartment

3.3.2.1 Predicted environmental concentrations

The predicted concentrations in soil are summarised in Table 3.21. The regional (steady-state) concentrations are:

- agricultural soil, 8.4 × 10–4 mg/kg wet weight
- natural soil, 9.7 × 10–8 mg/kg wet weight
- industrial soil, 9.7 × 10–8 mg/kg wet weight.

The above concentrations are estimated assuming the substance is not degradable. As discussed in Section 3.2.4 the actual degradation half-life for D4 in soil is uncertain. Example calculations assume a degradation half-life of D4 of six months, one year, and ten years (all at 12°C), and a degradation half-life of 2.3 days at 22°C [equivalent to a half-life of around five days at 12°C, based on the analysis of the soil degradation data carried out by Xu, as reported in CES (2005b); see Section 0]. The estimated concentrations that result are given in Table 3.22. Example calculations are given for one local scenario (personal care products – use by the general public; value given is the 30 day average value) and for the regional scenarios for agricultural soil and natural soil (this latter value is important as it acts as the regional background for the local soil concentrations).

Table 3.21 Predicted concentrations in soil

Scenario	PEC		
	Agricultural soil, 30 day average (mg/kg wet weight)	**Agricultural soil, 180 day average (mg/kg wet weight)**	**Grassland, 180 day average (mg/kg wet weight)**
Production and on-site use as an intermediate – UK site	7.3×10^{-5}	7.3×10^{-5}	7.3×10^{-5}
Off-site use as an intermediate – polymers – wet process – UK sites	3.0×10^{-4}	5.0×10^{-5}	1.0×10^{-5}
Off-site use as an intermediate – polymers – wet process – EU sites	1.4×10^{-6}	1.4×10^{-6}	1.4×10^{-6}
Off-site use as an intermediate – polymers – dry process – UK sites	2.5×10^{-7}	2.5×10^{-7}	2.5×10^{-7}
Off-site use as an intermediate – polymers – dry process – EU sites	2.7×10^{-5}	2.7×10^{-5}	2.7×10^{-5}
Off-site use as an intermediate – silica – UK and EU sites	8.1×10^{-7}	8.1×10^{-7}	8.1×10^{-7}
Personal care products – formulation – UK sites	1.0×10^{-6}	2.5×10^{-7}	1.3×10^{-7}
	2.9×10^{-6}	5.7×10^{-7}	1.9×10^{-7}
	7.4×10^{-7}	2.0×10^{-7}	1.2×10^{-7}
	9.5×10^{-7}	2.4×10^{-7}	1.3×10^{-7}
	3.7×10^{-6}	7.0×10^{-7}	2.2×10^{-7}
	6.4×10^{-6}	1.1×10^{-6}	3.1×10^{-7}
	1.4×10^{-5}	2.3×10^{-6}	5.5×10^{-7}
	4.3×10^{-6}	8.0×10^{-7}	2.4×10^{-7}
	3.5×10^{-6}	6.7×10^{-7}	2.1×10^{-7}
	3.6×10^{-6}	6.9×10^{-7}	2.2×10^{-7}
	4.0×10^{-6}	7.6×10^{-7}	2.3×10^{-7}
	3.2×10^{-6}	6.2×10^{-7}	2.0×10^{-7}
Personal care products – formulation – generic site (non-UK)	1.4×10^{-4}	2.3×10^{-5}	4.6×10^{-6}
Personal care products – use by general public	5.7×10^{-5}	9.6×10^{-6}	2.0×10^{-6}
Household products – formulation	4.5×10^{-5}	7.6×10^{-6}	1.6×10^{-6}
Household products – use	5.6×10^{-6}	9.5×10^{-7}	2.7×10^{-7}

Table 3.22 Example estimated concentrations of D5 in soils

Half-life at 12°C	Scenario	D5 concentration (mg/kg wet weight)
5 days	Local: personal care products – use	4.4×10^{-4}
	Regional: agricultural soil	1.2×10^{-6}
	Regional: natural soil	2.7×10^{-8}
6 months	Local: personal care products – use	9.2×10^{-4}
	Regional: agricultural soil	1.1×10^{-5}
	Regional: natural soil	3.1×10^{-8}
1 year	Local: personal care products – use	9.3×10^{-4}
12°C	Regional: agricultural soil	1.5×10^{-5}
	Regional: natural soil	3.2×10^{-8}
10 years	Local: personal care products – use	9.4×10^{-4}
	Regional: agricultural soil	5.1×10^{-5}
	Regional: natural soil	3.5×10^{-8}

As this example shows the predicted local concentration in soil is essentially independent of the degradation rate assumed, until a very rapid rate of degradation is assumed. The reason is that at the local level removal by volatilisation is dominant over the relatively short timescale considered in the calculations. However, at the regional level, a steady-state model is used whereby D4 volatilised from soil can subsequently be re-deposited by wet or dry deposition processes. Therefore, according to this model, re-deposition and degradation of the substance in soil compete with the volatilisation (and degradation in the atmosphere) when longer timescales are considered.

When a rapid rate of degradation for D4 (as may be expected under dry soil conditions) is included in the model, the predicted local concentration is reduced by a factor of around two compared with the situation in which no degradation in soil is assumed. This will be considered in relation to the risk characterisation for the terrestrial compartment.

As discussed in Section 0, the breakdown of PDMS polymers in soil may provide another route for exposure of soil organisms to D4. It is not possible to estimate reliably the amount of D4 in soil from such a process. However, a very rough indication of the potential significance of the process can be made.

Based on the monitoring data of Fendinger *et al.* (1997), a PDMS concentration of 5155 mg/kg sludge is likely to be towards the upper end of the actual PDMS concentrations in sewage sludge (see Section 0). The same approach is used as that in Section 0 along with the emission rate of 0.5 per cent over 25 weeks for cyclic siloxanes and other volatiles from the Lehmann *et al.* (1994) study. With the assumptions that D4 accounts for 25 per cent of the cyclic siloxanes and other volatiles and that, in this case, all of the D4 formed initially remains in the soil, a PDMS concentration of 5155 mg/kg sludge generates around 6 mg/kg sludge of D4 over the 25 week period, or an input of D4 via sludge into soil of 0.034 mg/kg sludge per day. Using the default sludge application rate given in the TGD (0.5 kg sludge/m^2, depth of agricultural soil 0.2 m, density of soil 1700 kg/m^3) this input rate converts into an

equivalent input rate of 0.017 mg/m^2/day or 5×10^{-5} mg/kg wet soil/day. This input can then be treated as a continuous input to soil using the methods outlined in the TGD (or input into the EUSES 2.0.3 program as a daily flux to soil), which then takes into account the subsequent volatilisation from soil. The PEC for soil (averaged over 30 days) that results is around 3×10^{-5} mg/kg wet weight (estimated using EUSES 2.0.3). This is well below the predicted regional concentration for D4.

3.3.2.2 Measured environmental concentrations

Spreading of sewage sludge that contains D4 onto soil is predicted to be a major route to soil, so it is relevant to consider the available data on the levels of D4 in sewage sludge.

Boehmer and Gerhards (2003) detected D4 at levels of 0.01–0.13 mg/kg dry weight in samples of sludge from three municipal WWTPs in Germany. The samples were collected in spring and summer 2000.

Kent *et al.* (1994) report that D4 was measured at a concentration of 0.21 mg/kg in sludge from a WWTP in the USA.

IUCLID (2005) reports the results of an unpublished study that found D4 at concentrations of <0.5, 0.08, and 0.18 mg/kg dry weight in three samples of sewage sludge cake from the USA.

Dewil *et al*. (2007) detected but not quantify D4 in a sample of waste-activated sludge collected from a WWTP in Coventry, UK. The sample was analysed as part of a study to develop a suitable methodology to analyse activated sludge samples.

Kaj *et al.* (2005) report the results of a survey of levels of D4 in sewage sludge samples from Sweden. The sampling and analytical methods used were designed to avoid both loss of D4 from the sample through volatilisation and contamination of the sample by D4. The sewage sludge samples were collected during 2004 from the anaerobic chambers of three large municipal sewage treatment plants in Stockholm, Gothenburg, and Borås, 51 further municipal sewage treatment plants from all over Sweden, and one industrial sewage treatment plant. D4 was detected in 37 of the 54 samples of municipal sludge. The mean, median, and maximum concentrations were 390, 310, and 2300 µg/kg dry weight, respectively. D4 was not detected (<120 µg/kg dry weight) in the sewage sludge from an industrial sewage treatment plant associated with a car manufacturer.

TemaNord (2005) recently also surveyed the levels of D4 in sewage sludge from Nordic countries. The samples were collected during 2004 and 2005 and the sampling and analytical methods used were designed to avoid both loss of D4 from the sample through volatilisation and contamination of the sample by D4. Two soil samples from landfill sites were also analysed in this study and the level of D4 was below the LOQ (<6 to <10 µg/kg dry weight). The results of the study are given in Table 3.23.

Table 3.23 Concentration of D4 in sewage sludge and soil samples from Nordic countries (TemaNord, 2005)

	Sampling location[1]	Concentration (µg/kg dry weight)
Faroe Islands	Havnardalur (disused landfill)	<10
	Husarhaga landfill (working landfill)	<6
	Sewage sludge	
Denmark	Kobenhavn, Lynetten STP (primary sludge)	740
	Kobenhavn, Lynetten (digested sludge)	470
Faroe Islands	Torshavn, Sersjantvikin	190
Finland	Nokia City, Kullonvuori STP (receives wastewater from several industries)	960
	Helsinki, Vilkinmäki STP (receives municipal, urban, and industrial wastewater)	230
	Espoo, Suomenoja STP (receives wastewater from perfume manufacturer and leachate from a landfill)	530
	Pormainen STP (receives municipal wastewater)	740
	Porvoo City, Kokonniemi STP (receives urban and industrial wastewater)	660
Iceland	Klettegardar STP	120
	Ananaust STP	96
Sweden	Skellefteå STP (digested sludge – no industrial inputs)	370
	Floda STP	120
	Ellinge STP (digested sludge – inputs from the food industry)	200
	Tekniska verket	380

Note: [1]STP, sewage treatment plant.

In the follow-up study Schlabach *et al*. (2007) investigated the levels of D4 in sewage sludge from two sewage treatment plants that discharge to the Inner Oslofjord in Norway (Bekkelaget STP and VEAS STP). The sampling and analytical methods used were designed to avoid loss of D4 from the sample through volatilisation and contamination of the sample by D4. The samples were collected in September 2006. The concentration of D4 in sewage sludge at the Bekkelaget STP was 1100 µg/kg dry weight in inlet sludge and 2700 µg/kg dry weight in outlet sludge. The concentration in sewage sludge at the VEAS STP was <180 µg/kg dry weight in inlet sludge and 1000 µg/kg dry weight in outlet sludge. These concentrations compare with those found in the TemaNord (2005) study. The influent and effluent water concentrations were also monitored at these plants, along with sediment concentrations close to the plants. The results of these analyses are summarised in Section 0.

3.3.2.3 Comparison of measured levels with predicted levels

The available data for D4 in sewage sludge from the EU show it was present at concentrations of 0.01–0.13 mg/kg dry weight in municipal WWTPs in Germany. Similar

levels are also reported in sewage treatment plants from the USA, and concentrations up to around 1 mg/kg dry weight (one sample had 2.7 mg/kg dry weight) are reported in sewage sludge levels from Nordic countries. The predicted levels of D4 in sewage sludge that result from consumer use in personal care products and household cleaning products are 2.3 mg/kg dry weight and 0.2 mg/kg dry weight, respectively.

The generally lower measured levels in sewage sludge samples could indicate that D4 is volatilised from sewage sludge during its collection and treatment (the calculations in EUSES assume that no further removal of D4 occurs once it is adsorbed onto the sludge, which may not be correct for a substance of high volatility). Alternatively, relatively few measured data points are available and so it is possible that actual levels could be higher at other plants than found in these surveys. If further volatilisation of D4 during the subsequent handling, transport, and spreading of sewage sludge does occur to a significant extent this has implications for the PECs for soil, as not all the D4 initially adsorbed onto the sludge during wastewater treatment will subsequently applied to land. This is considered further in Section 5.2.

3.3.3 Atmospheric compartment

3.3.3.1 Predicted environmental concentrations

The predicted concentrations in the air compartment are summarised in Table 3.24.

Table 3.24 Predicted concentrations in air

Scenario	Annual average PEC (mg/m^3)
Production and on-site use as an intermediate – UK site	0.046
Off-site use as an intermediate – polymers – wet process – UK sites	1.4×10^{-4}
Off-site use as an intermediate – polymers – wet process – EU sites	8.4×10^{-4}
Off-site use as an intermediate – polymers – dry process – UK sites	1.1×10^{-4}
Off-site use as an intermediate – polymers – dry process – EU sites	0.017
Off-site use as an intermediate – silica – UK and EU sites	4.6×10^{-4}
Personal care products – formulation – UK sites	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.4×10^{-5}
	1.5×10^{-5}
	1.6×10^{-5}
	1.4×10^{-5}
Personal care products – formulation – generic site (non-UK)	1.5×10^{-5}
Personal care products – use by general public	1.4×10^{-5}
Household products – formulation	1.4×10^{-5}

Household products – use	1.4×10^{-5}
Regional	1.4×10^{-5}

Mueller *et al*. (1995) predicted the atmospheric concentrations of D4 that result from use in consumer products in the USA. The atmospheric half-life assumed in the calculations is 15.9 days and the average D4 concentration predicted is 0.0032 µg/m^3 (3.2×10^{-6} mg/m^3) in the troposphere over continental USA, 0.0097 µg/m^3 (9.7×10^{-6} mg/m^3) in the surface atmosphere over continental USA, and 0.0013 µg/m^3 (1.3×10^{-6} mg/m^3) over the Atlantic Ocean.

3.3.3.2 Measured environmental concentrations

Boehmer *et al*. (2001) studied the levels of D4 in various air samples in the EU. The areas sampled included sites close to silicone production and use plants in Germany, France, and the UK, inside and around buildings in Germany, cities (Munich and Essen), and a rural area. The analytical method used had a detection limit of around 0.01 µg/m^3. Field blank samples were run at regular intervals. On occasions, traces of D4 were found in the blank analyses. In these cases the average blank value was subtracted from the field values, and the detection limit then set as twice the average blank value. The recovery of the method was in the range 112–116 per cent for D4 concentrations in the range 0.48–4.8 µg/m^3, which was considered acceptable given the low concentrations. The results of the analyses are summarised in Table 3.25.

Table 3.25 Concentration of D4 in air samples (Boehmer *et al.*, 2001)

Sample type	Total number of samples	D4 concentration (µg/m^3)			
		Minimum	Maximum	Median	90 percentile
Close to silicone plants (six locations)	58	<0.1	174	0.4	58
Inside and around buildings (three locations)	18	<0.1	5.0	0.1	1.4
City areas (two locations)	18	<0.1	0.3	<0.1	0.3
Rural area	6	<0.1	0.1	<0.1	<0.1

Wang *et al*. (2001) determined he levels of D4 in outdoor air in three cities in China (Guangzhou, Macau, and Nanhai). The samples were all collected between 9:00 am and 2:00 pm over a 20 minute period at a height of 1.2 m above ground. A blank sample was analysed with each batch and the analysis was considered acceptable when none of the target compounds were detected in the zero air test. The results for D4 are summarised in Table 3.26.

Table 3.26 Concentration of D4 in air from cities in China

City	Sample site	Number of samples	D4 concentration (µg/m^3)	
			Mean	Range
Guangzhou	Urban mixed areas	32	0.9	Not detected to 3.3
	Industrial area	8	13.5	6.4–20.5
	Landfill site	12	11.4	2.2–17.5
	WWTP	4	10.3	3.0–16.2
	Suburban area	18	0.4	Not detected to 1.6
	Forest park	2	Not detected	
Macau	Peninsula	10	3.0	0.8–4.3
	Taipai, University Campus	2	2.4 and 2.6 [1]	
	Coloane, coastal beach	2	0.2 and 0.3 [1]	
Nanhai	Three sites in small industrial towns, and one site in a rural area	24	0.9	Not detected to 3.5

Note: [1]Two samples only, for which values rather than the mean are reported.

Shields *et al.* (1996) investigated the levels of D4 in indoor air in three types of commercial buildings located throughout the USA. The buildings sampled included 50 telecommunications offices that were sparsely occupied, nine data centres with variable occupancy, and 11 densely occupied administrative offices. The samples were collected using passive diffusion samplers over a six week period from 18th March until 29th April 1991. Outdoor samples were collected from around the buildings at the same time. Three indoor and three outdoor samples were analysed at each location. Field blank and laboratory blank samples were also included. Occasionally, D4 was found in the blanks (the source of this contamination was thought to be from the carbon-impregnated Teflon® pad associated with the passive sampler). Where this occurred, corrections were applied based on the field blanks. The absolute detection limit for the analytical method used was around 0.05 µg/m^3, but the LOQ was set to 0.5 µg/m^3 (any substance present below this level was deemed 'not detectable'). The relative standard deviation of the method was typically 6–10 per cent. D4 was found in 92 per cent of the 50 telecommunications offices at a geometric mean concentration of 2.5 µg/m^3, all nine data centres at a geometric mean concentration of 9.4 µg/m^3, and all 11 administration offices at a geometric mean concentration of 10.2 µg/m^3. D4 was also found in 39 per cent of the 70 outdoor air samples at a geometric mean concentration of 0.1 µg/m^3. The levels in outdoor air are thought to reflect the influence of the building exhaust on the air levels close to the building rather than the general background concentration in air.

De Bortoli *et al*. (1986) carried out a survey of the levels of D4 in indoor air from homes in Northern Italy. Samples from six homes were collected during 1983 and 1984 over periods of four to seven days. D4 was found in two of the samples at concentrations of 10–13 µg/m^3. No quality-control details are given.

Brown and Crump (1998) found D4 in 37.5 per cent of homes sampled in an investigation of volatile organic carbon compounds in indoor air samples from 44 homes in Southampton. The samples were collected using diffusive sampling over a four week period. Blank diffusive

samplers were also analysed under the same conditions. No further quality-control details are given.

Wilkins *et al*. (1993) report D4 in office-dust samples collected by vacuum cleaner from nine city-hall buildings in Denmark. The samples were separated into the particle (<1 mm) and fibre fractions and siloxanes detected by a thermal desorption technique. D4 occurred in three of the nine samples analysed (the actual levels present are not given). No quality-assurance data are reported in the paper.

Ahearn *et al*. (1997) report that D4 was emitted from samples of cotton–polyester filters taken from the heating, ventilating, and air-conditioning system of a multi-story office building in the USA. No quality-control details are reported for the analysis.

Schweigkofler and Niessner (1999) measured D4 in biogas samples from two sewage treatment plants in Germany (concentration range ~2.9–7.0 mg/m^3 biogas). These concentrations relate to the concentration in the biogas itself rather than to the resulting concentration in the outdoor air.

TemaNord (2005) and Kaj *et al.* (2005) report the results of a survey of indoor air levels from 400 homes in Sweden. D4 was found in 73 homes at a concentration between 0.6 and 51.2 µg/m^3 (the mean of the detected concentrations is 9.0 µg/m^3).

Recently, Kaj *et al.* (2005) surveyed the levels of D4 in air in Sweden. The samples were collected during 2004 and 2005, and the sampling and analytical methods used were designed to avoid contamination by D4. The concentrations found in this survey are summarised in Table 3.27. Although some of the samples were collected from industrial areas, few details of the potential point sources are given, and it is not clear if D4 was actually being used in the area sampled.

Table 3.27 Concentration of D4 in air from Sweden (Kaj et al., 2005)

Location	Measured concentration (ng/m^3)	Comment
Råo	78	Background site
Råo	35	Background site
Råo	300	Background site
Stenungsund	51	Site near to potential point sources in an industrial area
Stenungsund	120	Site near to potential point sources in an industrial area
Stenungsund	230	Site near to potential point sources in an industrial area
Stockvik	71	Site near to potential point sources in an industrial area
Stockvik	18	Site near to potential point sources in an industrial area
Hudiksvallsgatan	84	Urban area of Stockholm
Hudiksvallsgatan	<23	Urban area of Stockholm
Hudiksvallsgatan	<97	Urban area of Stockholm

TemaNord (2005) carried out another survey of the levels of D4 in air in Nordic countries. The samples were collected in 2004 and 2005, and the sampling and analytical methods

used were designed to avoid contamination of the sample by D4. The results of this survey are summarised in Table 3.28.

The concentrations of D4 found in this survey were in the range 0.08–4.0 μg/m^3. The concentrations are generally elevated in urban areas and in areas close to sewage treatment plants compared to other areas.

Table 3.28 Concentration of D4 in air from Nordic countries (TemaNord *et al.*, 2005)

Sampling location		Concentration (μg/m^3)
Denmark	Jagtvejen	0.32
	Bjergmarken STP	0.66
	Sepstrup Sande	2.4
	H.C. Ørsted Institute	0.26
Faroe Islands	Torshavn, downtown	2.1
	Sersjantvikin STP	4.0
Finland	Nokia City STP	1.1
	Espoo landfill	0.29
Iceland	Reykjavik, urban	2.1
	Reykjavik, urban	0.32
	Reykjavik, urban	0.76
	Reykjavik, urban	0.4
Norway	Bekkelaget STP	1.0
	Bekkelaget STP	0.85
	Manglerud	0.55
	Oslo central station	0.58
Sweden	Högbytorp landfill (windside)	0.09
	Högbytorp landfill (windside)	0.08
	Mossarps recycling site	0.79
	Mossarps recycling site	1.1
	Göteborg, Kapellplatsen	0.14
	Göteborg, Kapellplatsen	0.35
	Stockholm, Hudiksvallsgatan	0.24
	Stockholm, Hudiksvallsgatan	0.18

Environment Canada (2008) gives the results of an unpublished study of the air levels of D4 in the Great Lakes region. In all 18 outdoor samples were collected from urban and rural areas in Ontario during February and March 2006, and D4 was found present in 'almost all of the samples' at concentrations <1 μg/m^3. Environment Canada (2008) also indicates that the widespread detection of D4 in ambient air could, in part, result from sample contamination as the methodology to determine trace concentrations in air is still under development.

3.3.3.3 Comparison of measured levels with predicted levels

From the data available the measured concentrations of D4 in air are up to around 174 μg/m^3 (median 0.4 μg/m^3) close to silicone plants. The predicted concentration for the UK site (46 μg/m^3) fits within this range.

At a regional level the concentrations of D4 in city areas in the EU are generally around 0.3 μg/m^3 (up to a maximum of around 2 μg/m^3), with the lower concentrations in rural areas (up to around 0.3 μg/m^3). These data are generally slightly higher than the concentrations

predicted for use of D4 by the general public and regional sources (around 0.01–0.02 µg/m^3). Possible explanations for this discrepancy could include underestimation of the loss from water, sediment, and soil through volatilisation, underestimation of the local and regional emissions to air, or overestimation of the rate of degradation of D4 in air when the concentrations in air are calculated. Another possible explanation is that the level of D4 usage in personal care products in the EU has fallen in recent years, and so the older monitoring data available may not represent the current levels.

Several studies also investigated the levels of D4 inside buildings. These levels are generally higher than those in the outdoor environment. However, such levels are not relevant to this assessment.

3.3.4 Food chain exposure

3.3.4.1 Predicted environmental concentrations

The predicted concentrations in fish and earthworms for secondary poisoning are summarised in Table 3.29.

For the concentration in fish, a measured BCF of 12,400 l/kg is used in the calculations. The TGD indicates that, as well as the bioconcentration, the BMF for fish should also be considered when the PEC for secondary poisoning is determined:

$$PECoral = PECwater \times BCF \times BMF \qquad (3.5)$$

In addition, the TGD suggests that the BMF value should be expressed on a lipid-normalised basis. As discussed in Section 3.2.9, a growth-corrected kinetic BMF of 4.6 on a growth-corrected and lipid-normalised basis was determined for the dietary exposure of fish to D4.

Equation (3.5) given in the TGD is not appropriate when actual data from laboratory feeding studies are considered because the default BMF values used in the TGD are not necessarily equivalent to those obtained in feeding studies. One of the intentions in the TGD is to model the concentration in fish that results from simultaneous exposure via both water and food, and this is represented Figure 3.2 and Equation (3.6).

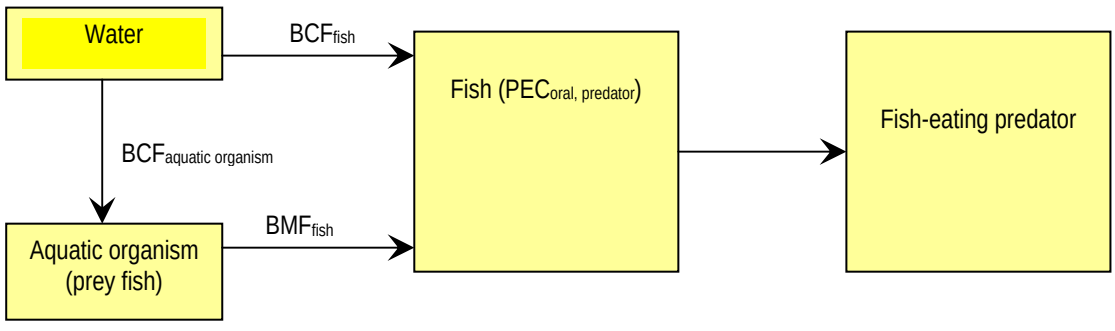

Figure 3.2 Model of the concentration in fish from simultaneous exposure via both water and food

$$PECoral, predator = (PECwater \times BCFaquatic\ organism \times BMFfish) + (PECwater \times BCFfish) \qquad (3.6)$$

Assuming that the ‘aquatic organism’ in the food chain is also a fish, Equation (3.6) simplifies to:

$$PEC_{oral,\ predator} = PEC_{water} \times BCF_{fish} \times (1 + BMF_{fish}) \quad (3.7)$$

Using a BMF of 4.6 for D4, Table 3.29 gives the PECs in predatory fish that result using Equation (3.7), assuming that 50 per cent of the exposure is from local sources and 50 per cent from regional sources (the default assumption in the TGD). However, there has been no formal discussion (or agreement) of this method of calculation at Technical Committee Meeting level. Also, this calculation should not be confused with the possibility of increasing concentrations found in sequential trophic levels (i.e. biomagnification) in the environment because the simplistic calculations used here neglect that the prey fish and/or organism also have a contribution from food. The calculation here simply takes into account that any given aquatic organism can be exposed via both water and food, and does not indicate possible trends in concentrations with increasing trophic level.

Table 3.29 Predicted concentrations in fish and earthworms

Scenario	PEC (mg/kg)	
	Fish[1,2]	Earthworms
Production and on-site use as an intermediate – UK site	112	0.048
Off-site use as an intermediate – polymers – wet process – UK sites	0.21	0.046
Off-site use as an intermediate – polymers – wet process – EU sites	0.17	0.044
Off-site use as an intermediate – polymers – dry process – UK sites	0.17	0.044
Off-site use as an intermediate – polymers – dry process – EU sites	0.17	0.045
Off-site use as an intermediate – silica - UK and EU sites	0.17	0.044
Personal care products – formulation – UK sites	0.17	0.044
	0.17	0.044
	0.17	0.044
	0.17	0.044
	0.18	0.044
	0.19	0.044
	0.21	0.044
	0.18	0.044
	0.18	0.044
	0.18	0.044
	0.18	0.044
	0.18	0.044
Personal care products – formulation – generic site (non-UK)	0.61	0.045
Personal care products – use by general public	0.39	0.045
Household products – formulation	0.31	0.045
Household products – use	0.19	0.044

Note: [1]The calculations for fish include a BMF of 4.6.
[2]Using the regional water concentration alone (2.4×10^{-3} µg/l) the concentration in fish is 0.17 mg/kg wet weight. Therefore many of the predicted local concentrations are dominated by the regional contribution.

The predicted concentrations in food for human consumption are summarised in Table 3.30.

Table 3.30 Predicted concentrations of D4 in food for human consumption

Scenario	PEC							Estimated total daily intake (mg/kg body weight/day)
	Fish (mg/kg)[1]	Root crops (mg/kg)	Plant leaves (mg/kg)	Meat (mg/kg)	Milk (mg/kg)	Drinking water (mg/l)	Air (mg/m^3)	
Production and on-site use as an intermediate – UK site	40	4.2×10^{-3}	1.9×10^{-3}	0.45	0.14	4.0×10^{-4}	0.046	0.082
Off-site use as an intermediate – polymers – wet process – UK sites	0.047	2.9×10^{-3}	5.6×10^{-6}	1.3×10^{-3}	4.2×10^{-4}	4.7×10^{-7}	1.4×10^{-4}	1.4×10^{-4}
Off-site use as an intermediate – polymers – wet process – EU sites	0.029	8.2×10^{-5}	3.5×10^{-5}	8.1×10^{-3}	2.6×10^{-3}	3.0×10^{-7}	8.4×10^{-4}	3.4×10^{-4}
Off-site use as an intermediate – polymers – dry process – UK sites	0.029	1.5×10^{-5}	4.6×10^{-6}	1.1×10^{-3}	3.5×10^{-4}	3.0×10^{-7}	1.1×10^{-4}	8.8×10^{-5}
Off-site use as an intermediate – polymers – dry process – EU sites	0.029	1.6×10^{-3}	7.0×10^{-4}	0.1 6	0.052	3.0×10^{-7}	0.017	6.0×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	0.029	4.7×10^{-5}	1.9×10^{-5}	4.5×10^{-3}	1.4×10^{-3}	3.0×10^{-7}	4.6×10^{-4}	2.1×10^{-4}
Personal care products – formulation – UK sites	0.031	1.5×10^{-5}	5.7×10^{-7}	1.4×10^{-4}	4.3×10^{-5}	3.1×10^{-7}	1.4×10^{-5}	5.5×10^{-5}
	0.033	3.3×10^{-5}	6.0×10^{-7}	1.4×10^{-4}	4.5×10^{-5}	3.3×10^{-7}	1.4×10^{-5}	5.9×10^{-5}
	0.030	1.2×10^{-5}	5.7×10^{-7}	1.4×10^{-4}	4.3×10^{-5}	3.0×10^{-7}	1.4×10^{-5}	5.5×10^{-5}
	0.030	1.4×10^{-5}	5.6×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.1×10^{-7}	1.4×10^{-5}	5.5×10^{-5}
	0.034	4.0×10^{-5}	5.7×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.4×10^{-7}	1.4×10^{-5}	6.0×10^{-5}
	0.037	6.6×10^{-5}	5.6×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.7×10^{-7}	1.4×10^{-5}	6.6×10^{-5}
	0.045	1.4×10^{-4}	5.6×10^{-7}	1.3×10^{-4}	4.3×10^{-5}	4.6×10^{-7}	1.4×10^{-5}	8.0×10^{-5}
	0.034	4.6×10^{-5}	5.6×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.5×10^{-7}	1.4×10^{-5}	6.2×10^{-5}
	0.034	3.9×10^{-5}	5.6×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.4×10^{-7}	1.4×10^{-5}	6.0×10^{-5}
	0.034	4.0×10^{-5}	6.0×10^{-7}	1.4×10^{-4}	4.5×10^{-5}	3.4×10^{-7}	1.5×10^{-5}	6.1×10^{-5}
	0.034	4.4×10^{-5}	6.6×10^{-7}	1.6×10^{-4}	4.9×10^{-5}	3.4×10^{-7}	1.6×10^{-5}	6.2×10^{-5}
	0.033	3.6×10^{-5}	5.6×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.3×10^{-7}	1.4×10^{-5}	6.0×10^{-5}
Personal care products – formulation – generic site (non-UK)	0.19	1.3×10^{-3}	6.0×10^{-7}	1.5×10^{-4}	4.7×10^{-5}	1.9×10^{-6}	1.5×10^{-5}	3.2×10^{-4}
Personal care products – use by general public	0.11	5.6×10^{-4}	5.8×10^{-7}	1.4×10^{-4}	4.5×10^{-5}	1.1×10^{-6}	1.4×10^{-5}	1.9×10^{-4}
Household products – formulation	0.082	4.4×10^{-4}	5.7×10^{-7}	1.4×10^{-4}	4.4×10^{-5}	8.3×10^{-7}	1.4×10^{-5}	1.4×10^{-4}
Household products – use	0.037	5.5×10^{-5}	5.6×10^{-7}	1.3×10^{-4}	4.2×10^{-5}	3.7×10^{-7}	1.4×10^{-5}	6.6×10^{-5}
Regional	0.029	0.055	5.6×10^{-7}	1.7×10^{-4}	5.5×10^{-5}	2.7×10^{-6}	1.4×10^{-5}	3.6×10^{-4}

Note: [1]The calculations for fish follow the methods given in the TGD and do not include a BMF.

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3.3.4.2 Measured environmental concentrations

Kaj *et al.* (2005) recently surveyed the levels of D4 in fish from Sweden. The samples were collected during 2004 and 2005, and the sampling and analytical methods used were designed to avoid both loss of D4 from the sample through volatilisation and contamination of the sample by D4. The concentrations found in this survey are summarised in Table 3.31. Fish muscle only was analysed in this study and D4 was not detected in any of the samples. Although some of the samples were collected from industrial areas, few details of the potential point sources are given, and it is not clear if D4 was actually being used in the area sampled. Sediment samples were also analysed from several of these locations. The sediment levels are reported in Section 0.

Table 3.31 Concentration of D4 in fish muscle from Sweden (Kaj *et al.*, 2005)

Location	Species	Measured concentration (µg/kg wet weight)	Comment
V. Fladen	Herring	<5	Background site
Ångsskärsklubb	Baltic herring	<5	Background site
Landsort	Baltic herring	<5	Background site
Stenungsund	Eelpout (females)	<5	Site near to potential point sources in an industrial area
	Eelpout (males)	<5	
	Eelpout (juveniles)	<5	
Sundsvall bay	Baltic herring	<5	Site near to potential point sources in an industrial area
	Herring	<5	
	Salmon	<5	
Lake Bäsingen	Not given	<5	
Lake Venjan	Not given	<5	
Ivösjön	Perch	<5	
Helsingborg	Flounder	<5	
Hammarsjön	Flounder	<5	
Storarydsdammen	Perch	<5	
Himmerfjärden	Perch	<5	
St Envättern	Perch	<5	
Lake Vänern, Åsfjorden	Perch	<5	
Lake Vänern, Kattfjorden	Perch	<5	

Kaj *et al.* (2005) also determined the levels of D4 in 49 samples of human breast milk. The detection limit for D4 in these samples was 2 µg/l, and D4 was found in three of the samples at a concentration of 2.9–10 µg/l.

TemaNord (2005) report D4 concentrations of <5–70 µg/kg fresh weight in biota from Nordic countries. The concentrations are generally elevated in urban areas and in areas close to sewage treatment plants, and only a few background samples show detectable levels. The sampling and analytical methods used were designed to avoid both loss of D4

from the sample through volatilisation and contamination of the sample by D4, and the samples were generally collected between 2002 and 2004 (fish and marine mammals) or 2000 and 2005 (bird eggs). The full results of this survey are summarised in Table 3.32.

Table 3.32 Concentration of D4 in biota from Nordic countries (TemaNord, 2005)

Sample type and location				Concentration (µg/kg wet weight)
Marine fish	Denmark	Roskildefjord	Three eelpout, liver	11
		Øresund	Three flounder, liver	13 [1]
		North Sea	Three flounder, liver	<5
		Wadden Sea	Three flounder, liver	<3
	Faroe Islands	Mylingsgrunnurin	Nine cod, liver	<5
		Kaldbaksfjøröur	Ten sculpin, liver	<5
		Kaldbaksfjøröur	19 flatfish (dab), liver	<5
	Norway	Lista/Farsund	16 cod, liver	<5
		Indre Sørfjord	10 cod, liver	12[a]
		Ulsteinvik	5 cod, liver	11[a]
		Indre Oslofjord	4 cod, liver	70
Freshwater fish	Faroe Islands	Lake A Myranar	Ten Arctic char, liver	<5
		Lake A Myranar	Seven brown trout, liver	<5
	Finland	Old City Bay, Helsinki	Two pike, liver	5.8[a]
		Old City Bay, Helsinki	Two pike, liver	5.7[a]
		Old City Bay, Helsinki	Two pike, liver	8.9[a]
		Cold Water Bay, Helsinki	Two pike, liver	<5
		Guard Village Bay, Helsinki	Two pike, liver	<5
	Norway	Lake Mjøsa	Five vendance, liver	<5
	Sweden	River Nissan, Skepshult	One pike, liver	<5
		River Nissan, Rydöbruk	One pike, liver	<5
Marine mammals	Denmark	Coastal area, Øresund	Five seals, blubber	<5
		Samsø	Five seals, blubber	<5
		Limfjorden	Five seals, blubber	<5
		Hesselø	Five seals, blubber	12[a]
	Faroe Islands	Sandangeröi	Ten pilot whales, blubber	<5
		Gøtu	Ten whiteside dolphins	<5
	Iceland		Five common porpoise	<5
Seabird eggs	Faroe Islands	Skúvoy	Ten fulmar eggs	<5
		Koltur/Skúvoy	Ten black guillemot eggs	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
	Sweden	Söderskäretskan	One herring gull egg	<5

	Svartlögafjorden	One herring gull egg	<5
	Svartlögafjorden	One herring gull egg	<5
	Svartlögafjorden	One herring gull egg	<5
	Svartlögafjorden	One herring gull egg	<5
	Svartlögafjorden	One herring gull egg	<5

Note: [1]Concentrations are above the limit of detection, but below the LOQ.

In the follow-up study Schlabach *et al*. (2007) investigated the levels of D4 in biota from the Inner Oslofjord in Norway [where the highest concentration of D4 was found in cod liver in the TemaNord (2005) study]. The samples investigated included common mussels, flounder fillet, flounder liver, cod liver, and cod stomach content (mainly krill, shrimp, and small crabs). The sampling and analytical methods used were designed to avoid loss of D4 from the sample through volatilisation and contamination of the sample by D4. All the samples were collected between September and November 2006. The mussels were immersed in clean water for one hour prior to analysis to allow detrital material to depurate. The levels found are summarised in Table 3.33.

Table 3.33 Concentration of D4 in biota from the Inner Oslofjord (Schlabach et al., 2007)

Sample	Location	Concentration	
		µg/kg wet weight	µg/kg lipid
Common mussel	Færder	1.9	84
	Gressholmen	2.3	439
	Ormøya	1.3	130
Flounder liver	Frognerkilen	2.6	16
Flounder fillet	Frognerkilen	1.9	139
Cod liver (each sample is a pooled sample from five individual fish)	Nesodden/Vestfjord	134	860
	Nesodden/Vestfjord	121	490
	Nesodden/Vestfjord	81	244
Cod stomach content	Nesodden/Vestfjord	5.0	283
	Nesodden/Vestfjord	7.4	372
	Nesodden/Vestfjord	9.3	474

D4 was found in all the biota samples analysed. The highest levels found are in cod liver, and the concentrations in cod liver (81–134 µg/kg wet weight) compare with those in cod liver from the same area in the TemaNord (2005) survey (70 µg/kg wet weight; sample collected in 2004).

EVONIK Industries (2007) briefly reported in a slide presentation the results of a further survey of the levels of D4 in freshwater and marine fish from Europe. The analytical detection limit was 20 µg/kg wet weight. In the marine fish, D4 was not detected in samples of 11 species from the North East Atlantic, six species from the Baltic Sea close to the mouth of the Odra River, and one species from the Baltic Sea close to Estonia. For the freshwater fish, D4 was not detectable in three species from Lake Nipgård, Denmark, and in three species from Lake Constance, Germany. D4 was found at concentrations between 100 and 900 µg/kg wet weight in samples of roach, ide, and eel from the River Rhine, Germany (close to the Dutch Border). The results, including details of the species analysed, are summarised in Table 3.34. Few other details of this study are currently available.

Table 3.34 Concentration of D4 in freshwater and marine fish from Europe (EVONIK Industries, 2007)

Location	Species	Measured concentration (µg/kg wet weight)	Comment
River Rhine, Germany (close to Dutch border)	Roach (Rutilus rutilus)	170	
	Ide (Leuciscus idus)	100	Two samples analysed with 100 µg/kg in each
	Eel (Aguilla aguilla)	400-900	Two samples analysed and various tissues were also analysed separately; concentrations were 100 µg/kg in liver, 200 µg/kg in skin, 1000 µg/kg in fatty tissue, and 700 µg/kg in muscle
Lake Constance, Germany	Lake white fish (Coregonus spp)	<20	
	Alpine charr (Salvelinus umbla)	<20	
	Eel (Aguilla aguilla)	<20	
Lake Nipgård, Denmark	Perch (Perca fluviatilis)	<20	
	Roach (Rutilus rutilus)	<20	
	Pike (Esox lucius)	<20	
North East Atlantic	Atlantic salmon (Salmo solar)	<20	Sample from Denmark fjord
	Cod (Gadus morhua)	<20	
	Common sole (Solea solea)	<20	
	Pilchard (Sardina pilcharus)	<20	
	Redfish (Sebastes marinus)	<20	
	Wolffish (Anarhichas lupus)	<20	
	Mackerel (Scomber scombrus)	<20	
	Plaice (Pleuronectes platessa)	<20	
	Monkfish (Lophius piscatorius)	<20	
	Lemon sole (Microstomus kitt)	<20	
	Pollock (Pollachius virens)	<20	
Baltic Sea (close to mouth of Odra River, Germany)	Eel (Aguilla aguilla)	<20	
	Flounder (Platichthys flesus)	<20	
	Turbot (Psetta maxima)	<20	
	Perch (Perca fluviatilis)	<20	
	Pike-perch (Stizostedion lucioperca)	<20	

	Pike (Esox lucius)	<20	
Baltic Sea, Estonia	Pike-perch (Stizostedion lucioperca)	<20	

Boehmer *et al*. (2007) carried out a preliminary screening study of the levels of D4 in mussels from the southern North Sea. The main purpose of the study was to develop methodologies to collect, transport, prepare, and analyse mussel tissue samples for cyclic VMSs. The methodology was developed to prevent both contamination with D4 and loss of D4 during the collection and analytical procedure. Around 30–50 blue mussels (*Mytilus edulis*) were collected from intertidal areas from sites at Rømø and Ho Bugt (Denmark), Norderney (Germany), Ameland (the Netherlands), and Ambleteuse and Cap Gris Nez (France). Samples of sediment (three samples of the top 5 cm from each location) and surface water (collected from shallow puddles) were also collected at the same locations as the mussels. The mussels were placed in clean water for 24–40 hours prior to analysis to purge sediment particles from the mussels. Samples of mussels (total weight 10 g, each sample consisted of 2–6 individuals) were then analysed. The method detection limit was 6 µg/kg, and the method LOQ was 22 µg/kg. In all, 23 samples were analysed. The levels found (corrected for the levels of D4 found in laboratory blank samples) are below the method detection limit (<6 µg/kg) in all of the samples analysed.

Wallace *et al*. (1984) detected D4 in drinking water from the USA. The levels found are not reported.

3.3.4.3 Comparison of measured levels with predicted levels

Relatively few data are available for the measured levels of D4 in biota. D4 is not detectable in the majority of the fish and bird egg samples analysed. However, D4 was detected at concentrations of up to 134 µg/kg wet weight in livers of some marine and freshwater fish, and in one composite blubber sample from seals. Another survey reports levels up to 900 µg/kg wet weight in freshwater fish from the River Rhine, but found that D4 was generally not detectable in marine fish.

Although it is not possible to compare the predicted levels for whole fish directly with those for a specific organ (e.g. liver), the predicted levels of D4 in fish for secondary poisoning in some scenarios are generally of a similar order of magnitude to the highest levels actually measured. Also, it is not clear how the sampling locations for the measured biota samples actually relate to the scenarios considered in this assessment and so it is not possible to make a more detailed comparison of the predicted and measured levels. The most relevant data with which to compare the PECs are probably the recent data available for the River Rhine, as these are likely to be influenced by local sources of release. The levels found in this survey were between 100 and 900 µg/kg wet weight, which compares with the PECs from the majority of local scenarios (PECs are in the range 170–112,000 µg/kg wet weight, with most in the range 170–610 µg/kg wet weight).

3.3.5 Marine compartment

3.3.5.1 Predicted environmental concentrations

The predicted concentrations relevant for the marine environment are summarised in Table 3.35. The calculations assume that the emissions to wastewater are not treated in a WWTP (this is the default assumption for the marine risk assessment in the TGD), except for

scenarios in which site-specific information is available that shows the effluent from the site does pass through a WWTP and scenarios for personal care products – use and household products – use (in which the WWTP is the local emission source).

Similar to the situation for secondary poisoning described in Section 0, the methodology in the TGD is modified to allow the estimated BMF for D4 from food uptake to be used. The intention in the TGD is to model the concentration in fish that results from simultaneous exposure via both water and food in a simplified food chain. An example scheme that can utilise the available food-uptake data is presented in Figure 3.3. This scheme differs from that in the TGD, in which the top predator could be a predatory mammal or bird that feeds on other marine mammals or birds (a different equation needs to be constructed for such food chains). However, the scheme in Figure 3.3 allows the available food-uptake data for D4 by fish to be used in an extended food chain.

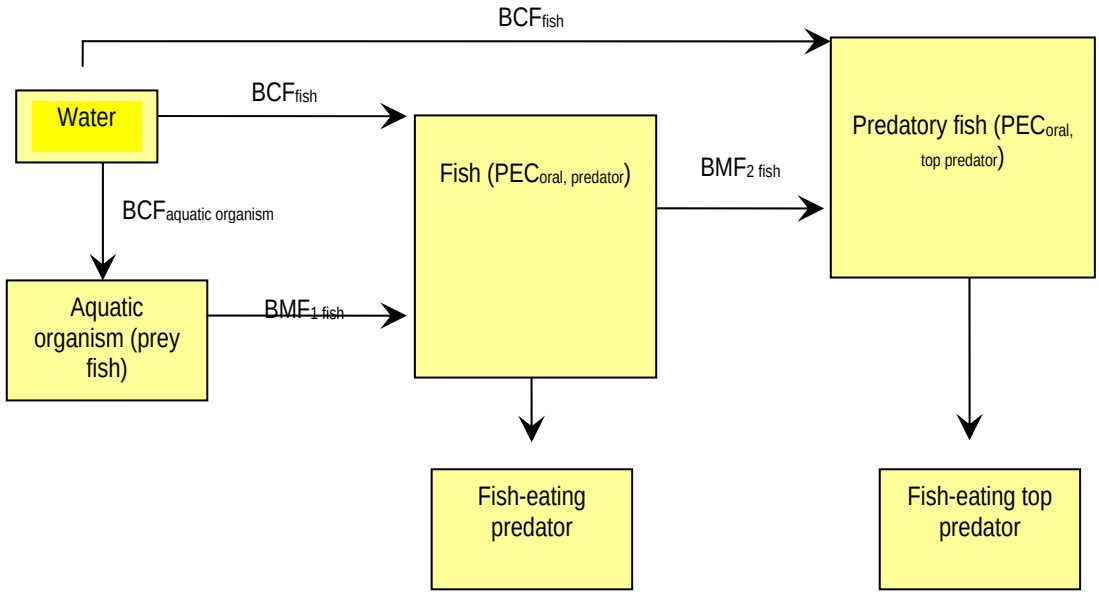

Figure 3.3 Model of the concentration in fish from simultaneous exposure via both water and food in a simplified food chain

Assuming that the 'aquatic organism' in the food chain is also a fish, the appropriate equations for this scheme are:

PECoral, predator = (PECwater × BCFaquatic organism × BMF1 fish) + (PECwater × BCFfish) (3.8)

and

PECoral, top predator = (1 + BMF1 fish) × (1 + BMF2 fish) × BCFfish × PECwater (3.9)

Using a BMF of 4.6, as before, for both BMF1 and BMF2, the PECs for predators and top predators that result from Equations (3.8) and (3.9), respectively, are given in Table 3.36. These calculations assume that for predators 50 per cent of the exposure is from local sources and 50 per cent from regional sources, and that for top predators 10 per cent of the exposure is from local sources and 90 per cent from regional sources (the TGD defaults).

Table 3.36 Predicted concentrations relevant to the marine environment

Scenario	PEC			
	Water (µg/l)	Sediment (mg/kg wet weight)	Predators[1] (mg/kg)	Top predators[1] (mg/kg)
Production and on-site use as an intermediate – UK site	0.099	0.037	2.8	3.2
Off-site use as an intermediate – polymers – wet process – UK sites	3.6×10^{-3}	1.3×10^{-3}	0.044	0.10
Off-site use as an intermediate – polymers – wet process – EU sites	1.6×10^{-4}	6.0×10^{-5}	0.011	0.063
Off-site use as an intermediate – polymers – dry process – UK sites	1.6×10^{-4}	6.0×10^{-5}	0.011	0.063
Off-site use as an intermediate – polymers – dry process – EU sites	1.6×10^{-4}	6.0×10^{-5}	0.011	0.063
Off-site use as an intermediate – silica – UK and EU sites	1.6×10^{-4}	6.0×10^{-5}	0.011	0.063
Personal care products – formulation – UK sites	1.7×10^{-4}	6.4×10^{-5}	0.012	0.063
	1.9×10^{-4}	7.2×10^{-5}	0.012	0.064
	1.7×10^{-4}	6.3×10^{-5}	0.011	0.063
	1.7×10^{-4}	6.3×10^{-5}	0.012	0.063
	2.0×10^{-4}	7.5×10^{-5}	0.012	0.064
	2.3×10^{-4}	8.7×10^{-5}	0.013	0.065
	3.2×10^{-4}	1.2×10^{-4}	0.016	0.068
	2.1×10^{-4}	7.8×10^{-5}	0.013	0.064
	2.0×10^{-4}	7.5×10^{-5}	0.012	0.064
	2.0×10^{-4}	7.5×10^{-5}	0.012	0.064

	2.1×10^{-4}	7.7×10^{-5}	0.013	0.064
	2.0×10^{-4}	7.3×10^{-5}	0.012	0.064
Personal care products – formulation – generic site (non-UK)	0.044	0.016	1.3	1.5
Personal care products – use by general public	8.2×10^{-4}	3.0×10^{-4}	0.034	0.088
Household products – formulation	0.015	5.5×10^{-3}	0.43	0.53
Household products – use	2.2×10^{-4}	8.2×10^{-5}	0.013	0.065
Regional	1.6×10^{-4}	1.1×10^{-4}	0.011	0.062

Note: [1]For both predators and top predators the value for BMF_1 and BMF_2 is 4.6.

3.3.5.2 Measured environmental concentrations

The available measured levels of D4 in marine water are given in Section 0. Relatively few data are available, but these show that the levels in marine water taken from the mouth of the River Mersey and from Cardiff Bay are below the detection limit (0.2 and 0.04 µg/l, respectively). D4 was, however, found in marine sediment samples at concentrations of 0.028–0.047 mg/kg dry weight from Cardiff Bay, but it was not detected (<0.003 mg/kg dry weight) in samples from the mouth of the River Mersey. More recent data from Nordic countries show D4 in one marine sediment at a concentration of 84 µg/kg dry weight, but it was generally not detectable in other marine sediments and in marine waters.

The available monitoring data for marine biota are given in Section 0. D4 was detected at concentrations up to 134 µg/kg wet weight in livers of some marine fish, and also at low concentrations (close to the detection limit) in blubber of marine mammals (seals). In contrast, D4 was not detected in seabird eggs.

3.3.5.3 Comparison of measured levels with predicted levels

Relatively few data are available on the levels of D4 in marine waters. It is generally not detectable in marine water, but it was found in some marine sediment samples. As discussed in Section 0, a level of D4 in sediment of 0.047 mg/kg dry weight is equivalent to a concentration of around 0.010 mg/kg on a wet weight basis using the default value for the water content of sediment from the TGD. Similarly, monitoring data for Nordic countries show a slightly higher level of D4 in sediment of 0.084 mg/kg dry weight (equivalent to a concentration of around 0.018 mg/kg on a wet weight basis). These levels are reasonably consistent with some of the values predicted, but it is not possible to make a more meaningful comparison directly with the scenarios considered in this assessment because the levels in the areas sampled may be influenced by a number of sources.

For the marine biota, the levels measured in fish livers (up to 134 µg/kg wet weight) are reasonably consistent with the concentrations predicted in predators and top predators, but the predicted concentrations relate to whole-body concentrations rather than to concentrations in specific organs. Also, although D4 was found in some samples of fish, in a large proportion of the samples D4 was not detectable. Again, it is not possible to make a more meaningful comparison of the predicted and measured levels, as it is not clear how the areas sampled relate to the scenarios considered in this assessment.

4 Effects assessment: Hazard identification and dose (concentration) versus response (effect) assessment

4.1 Aquatic compartment (including sediment)

Many of the aquatic toxicity data available for D4 were generated in response to recommendations from the ITC under the US TSCA (Walker and Smock, 1995) and so have undergone a peer review process in the United States. Much of this information has now been published in review articles in the open literature (e.g. Sousa *et al*., 1995; Chandra, 1997). The essential details of the tests are reported here as many of the tests were carried out using modified test systems (e.g. with no headspace) to address the inherent problems of testing D4 (low water solubility, high volatility) and it is important to understand the precautions taken to ensure concentrations were maintained during the test when selecting the most appropriate data for use in the risk assessment. These details are generally taken from the published reviews of the data and in a few cases the original laboratory test reports.

4.1.1 Toxicity to fish

4.1.1.1 Short-term studies

The available short-term toxicity of D4 to fish is summarised in Table B1 and

Table B2 in Appendix B.

Sousa *et al.* (1995) investigated the toxicity of D4 to a freshwater fish (rainbow trout, *O. mykiss*) and a marine fish (sheepshead minnow, *Cyprinodon variegatus*) in a prolonged acute toxicity study (14 days) using a flow-though system with no head space (to prevent loss from volatilisation). The D4 tested was >99 per cent pure and stock solutions of it were prepared daily by slow-stirring dilution water with a floating layer (approximately 6 mm thick) of D4. This method of stock-solution preparation gives reproducible results and can achieve a maximum concentration of ~30 µg/l in soft freshwater and ~6 µg/l in seawater (30‰). The stock solutions, and 50–60 per cent dilutions thereof, provided five exposure concentrations, and the flow rates gave around six volume changes per day. The actual concentration of D4 in the test vessels was measured at regular intervals during the test. The mean measured concentrations in the five exposure groups used in the rainbow trout

test were 2.9, 4.4, 6.9, 12, and 22 µg/l and the mean measured concentrations in the five exposure groups used in the sheepshead minnow test were1.3, 1.6, 2.3, 4.2, and 6.3 µg/l. Treatment-related mortalities occurred in the study with rainbow trout, but no mortalities occurred in any treatment group until day seven. By day 14, around 80 per cent mortality occurred in the fish exposed to 22 µg/l, with 75 and 20 per cent mortality those exposed at 12 and 6.9 µg/l. No mortality occurred at exposure concentrations of 4.4 and 2.9 µg/l. The lethal concentration that kills 50 per cent of the population in 14 days (14 day LC_{50}) was 10 µg/l and the 14 day NOEC was 4.4 µg/l, both based on measured concentrations.

The trout used in this test had a mean weight and mean length of 0.42 g and 37 mm, respectively. Further (unpublished) studies were carried out, using a similar test system, to investigate the effect of the size of the trout on the toxicity of D4. These experiments confirmed the above results when fish of <1.0 g were used, but studies with larger rainbow trout (mean weight 4.3 g) and fathead minnows (*P. promelas*, mean weight 1.7 g) showed no toxicity at levels up to the solubility limit of D4 in the test medium. A further test (again unpublished) with larger rainbow trout (mean weight 2.2 g), but in which D4 was injected directly into the influent water of the test system (to give a concentration of 39 µg/l) also showed very little toxicity over 14 days of exposure. It is concluded that smaller fish appear to be more sensitive to D4 than larger fish.

In the test with sheepshead minnow, no treatment-related mortality occurred at any exposure concentration, therefore the 14 day NOEC was ≥6.3 µg/l (the highest measured concentration tested). The fish used in this test had a mean weight and mean length of 0.33 g and 26 mm, respectively.
IUCLID (2005) gives the results of a second 14-day flow-through study with rainbow trout. The study is unpublished and so only a summary of the results is currently available. The test was carried out using five measured concentrations of 5.7, 9.4, 16.9, 34.2, and 51.7 µg/l. It is reported that on days 12–14 of the study there was a malfunction of the dosing system, which resulted in concentrations higher than the functional water solubility of D4 in the system used (estimated as 36.8 µg/l). During this period five out of ten fish exposed to the concentrations at or above this limit showed unusual swimming behaviour characteristic of narcosis. The NOEC from this study was 16.9 µg/l based on measured concentrations. It is possible that this study is one of the supplementary studies referred to by Sousa *et al.* (1995).
IUCLID (2005) also reports the results of an 18-day prolonged acute toxicity study with rainbow trout of various sizes. The LC_0 for the larger fish (5 g) was >31 µg/l, but small fish were more sensitive (LC_{80} = 23 µg/l). No further details of this test are currently available, but it is possible that this study is one the supplementary studies referred to by Sousa *et al.* (1995).

IUCLID (2005) summarises a number of other short-term toxicity tests (both published and unpublished) carried out with D4 and both freshwater and marine fish. These were generally at concentrations well in excess of the water solubility of D4, often in static open systems in which the loss via volatilisation is appreciable. The results include a 96 hour LC_0 of 200 mg/l and a 96 hour LC_{50} of >1041 mg/l for *Leuciscus idus* (unpublished studies), a 96 hour LC_{50} >1000 mg/l for *Lepomis macrochirus* (Firmin *et al.*, 1984), a 96 hour LC_{50} >1000 mg/l for *O. mykiss* (Firmin *et al.*, 1984), 96 hour LC_{50}s >500 mg/l and >1000 mg/l for *Fundulus heteroclitus* (Firmin *et al.*, 1984). Taken as a whole, these results cannot be considered valid for use in the risk assessment because of the large uncertainty over the actual (dissolved) exposure concentrations in these tests.

4.1.1.2 Long-term studies

The available long-term toxicity of D4 to fish is summarised in

Table B3 in Appendix B.

Following on from the results from the prolonged acute study with *O. mykiss* (see Section 0), Sousa *et al*. (1995) carried out a 93 day early lifestage study was with the same species. The stock solution preparation and test system used were similar to the prolonged acute study, but the flow rate was increased to give approximately 7.6 volume replacements per day. In all, five concentrations were tested (mean measured concentrations were 0.25, 0.53, 1.1, 1.9, and 4.4 µg/l), plus a control. The experiment started with fertilised eggs (two hours after fertilisation) and continued until 60 days post hatch. Hatching was completed by day 33. On day 19 of the experiment embryo viability was 71–79 per cent in the exposed groups and 77 per cent in the controls. It is concluded that no statistically significant (p = 0.05) treatment-related effects occurred in development or time to hatch. At the end of hatching, survival of the organisms ranged from 79 per cent to 85 per cent in the exposed groups, compared to 80 per cent in the control. Again, no statistically significant treatment-related effects were observed in this endpoint. At the end of hatching approximately 1 per cent (seven individuals) of the surviving larvae had various degrees of spinal curvature. These larvae were randomly distributed among the treatment levels (two each in the 1.9 µg/l and 0.53 µg/l treatment groups, and one in the 0.25 µg/l treatment group) and the control (two), and so were not thought to be treatment-related.

The larvae showed signs of swim-up on day 46 of the experiment (13 days post-hatch) and by day 54 >95 per cent of the surviving larvae in all treatment groups and control exhibited swim-up behaviour. No treatment-related effects on swim-up were apparent.
The survival of larvae during the post-hatch exposure was determined over two periods (day 0 to day 45 and day 45 to day 60). Survival in larvae over the day 0 to day 45 period was 90–100 per cent in the treatment groups (97 per cent in the control) and that over the day 45 to day 60 period was 98–100 per cent in the exposed groups (100 per cent in the control). It is concluded that no statistically significant effects were seen on larval survival. Further, no statistically significant treatment–related effects on growth (as measured by total length and wet weight) of the larvae occurred by the end of the study.

Overall, it is concluded that no treatment-related effects occurred in this study and so the 93 day NOEC is ≥4.4 µg/l (the highest concentration tested).

4.1.2 Toxicity to aquatic invertebrates

4.1.2.1 Short-term studies

The available short-term toxicity of D4 to aquatic invertebrates is summarised in

Table B4 (freshwater) and

Table B5 (marine) in Appendix B.

Sousa *et al.* (1995) studied the acute toxicity of D4 to the freshwater invertebrate *Daphnia magna* (48 hour study) and the marine invertebrate *Mysidopsis bahia* (96 hour study) using a flow-through system with no head space. The D4 tested was >99 per cent pure and stock solutions of the substance were prepared daily (*M. bahia*) or every 48 hours (*D. magna*) by slow-stirring dilution water with a floating layer (approximately 6 mm thick) of D4. This method of stock-solution preparation gives reproducible results and can achieve a maximum concentration of ~15 µg/l in hard freshwater and ~9.1 µg/l in seawater (20‰). The stock solutions, and 50–60 per cent dilutions thereof, provided five exposure concentrations and the flow rates gave around six (*M. bahia*) or 8–10 (*D.* magna) volume changes per day. The actual concentration of D4 in the test vessels was measured at regular intervals during the test.

No mortalities or immobilisation occurred at any treatment level with *D. magna* over 48 hours of exposure. The 48 hour 50 per cent effect concentration (EC_{50}) was therefore >15 µg/l and the 48hour NOEC was ≥15 µg/l.

Similarly no mortalities or immobilisation occurred at any treatment level with *M. bahia* over 96 hours of exposure. The 96 hour LC_{50} was therefore >9.1 µg/l and the 96 hour NOEC was ≥9.1 µg/l.

IUCLID (2005) summarises a number of other short-term toxicity tests (both published and unpublished) carried out with D4 and invertebrates. These were generally carried out at concentrations well in excess of the water solubility of D4, and it is unlikely that precautions were taken against loss from volatilisation. The results include a 24 hour EC_{50} of 25.2 mg/l for *D. magna* (unpublished study), a 24 hour EC_{50} >500 mg/l with *Artemia salina* (Firmin *et al.*, 1984), and a 96 hour EC_{50} >1000 mg/l for *Crangon crangon* of (Firmin *et al.*, 1984). Taken as a whole, these results cannot be considered valid for use in the risk assessment because of the large uncertainty over the actual (dissolved) exposure concentrations in these tests.

4.1.2.2 Long-term studies

The available long-term toxicity studies are summarised in Table B6 in Appendix B. Following on from the acute toxicity study with *D. magna* reported in Section 0, Sousa *et al.* (1995) carried out a 21 day reproduction study using a similar test system as that for the acute study (i.e. no headspace). Five exposure concentrations were used (measured concentrations were 1.7, 1.8, 4.2, 7.9, and 15 µg/l).

This study showed a statistically significant (p = 0.05) reduction in the survival at the highest concentration tested (survival in the 15 µg/l was 77 per cent) compared with the control population (survival was 93 per cent) after 21 days. The 21 day NOEC for the survival endpoint is therefore 7.9 µg/l.

For the reproduction endpoint, the mean cumulative number of offspring per female daphnid was 111 in the control, 107, 92, 123, 151, and 167 in the 1.7 µg/l, 1.8 µg/l, 4.2 µg/l, 7.9 µg/l, and 15 µg/l treatment groups, respectively. There were no statistically significant (p = 0.05) differences between the control response and the treatment response in the 1.7, 1.8, and 4.2 µg/l groups, but the mean cumulative number of offspring per female was significantly higher in the 7.9 µg/l treatment group than in the control groups (the data for the 15 µg/l treatment group were not included in the statistical analysis as a reduction in daphnid survival occurred in this group). Therefore it is concluded that concentrations of D4 ≤7.9 µg/l do not adversely affect the reproduction of *D. magna.*

The overall 21 day NOEC from this study is therefore 7.9 µg/l based on the survival endpoint. Kent *et al*. (1994) and Springborn Laboratories (1991a) investigated the toxicity of D4 to *C. tentans*, both in water-only exposure and in sediment exposures..

The D4 tested (purity of 99 per cent) was mixed with ^{14}C-D4. The tests were carried out using a flow-through system with no headspace (to minimise loss of D4 through volatilisation). The test solution was D4-saturated water prepared by maintaining a layer of D4 on top of 195 l of gently stirred dilution water for 24 hours (fresh solutions were prepared daily). The D4 concentration in these stock solutions was 20–30 µg/l. The volume of the test vessels used was 3.8 litres and a thin (2 mm) layer of sediment (previously heated for four hours at 600°C to remove the organic carbon content) on the bottom allowed the organisms to construct tubes (to minimise stress). Second instar larvae were used, with 50 per treatment. During the test the larvae were fed a flaked fish-food suspension daily.

The endpoints determined in the study were survival and growth (wet weight) of the midge larvae. The normal life cycle of the test species includes a progression through several benthic instar stages followed by a pupae stage at which the developing larvae float to the water surface and obtain their oxygen requirements directly from air. However, as there was no headspace in the tests, once the organisms reached this stage they suffocated. Therefore the criteria used to assess survival were modified to take this into account (i.e. the dead organisms in the pupae or adult stage were taken as positive indicators of organism survival at the stages up to this point). Only the organisms found dead in the larval stages or missing at test termination were considered dead (see also Section 4.1.8).

Five concentrations were tested (mean measured concentrations were 0.49, 1.2, 2.9, 6.5, and 15 µg/l), along with a control, and the total exposure was for 14 days. No statistically significant (p = 0.05) effects were noted on mean survival or mean organism wet weight in this study. Therefore the 14 day NOEC from the study is ≥15 µg/l.

4.1.3 Toxicity to aquatic plants and algae

The toxicity of D4 to aquatic plants and algae is summarised in

Table B7, Appendix B.

IUCLID (2005) gives details of a study (unpublished) on the toxicity of D4 to algae (*Pseudokirchneriella subcapitata*[20]). In the test, algae were exposed to a saturated solution of D4 in a sealed system with no headspace. The initial measured concentration was 22 µg/l, but this declined to <1 µg/l after 24 hours, presumably because of adsorption onto the algal cells. At this concentration the growth rate decreased by 18 per cent compared to the control growth rate. However, the growth rate in the control was lower than expected (a control in a standard open test system was included in the experiment for comparison), which indicates that the restricted oxygen or CO_2 in the sealed system may have restricted the growth in the test. Based on this, the result is considered not to be valid for use in the risk assessment.

A second algal test carried out by Firmin *et al*. (1984) is summarised in IUCLID (2005). The 14-day EC_{50} for *Anabaena flos-aquae* (based on ash-free weight and filament count) was >2000 mg/l. However, the very high test concentrations used, the apparent lack of controls used to limit volatilisation of D4, and the length of the test (the cells were unlikely to be in exponential growth throughout the course of the test) means that the result is considered as not valid for use in the risk assessment.

[20] Formerly known as *Selenastrum capricornutum*.

4.1.4 Quantitative structure–activity relationships

Estimates for the toxicity of D4 are generated from the measured value of the log K_{ow} value (log K_{ow} = 6.49) using the equations outlined in the TGD. The estimates obtained are summarised in Table 4.1, as are the equivalent estimates using a log K_{ow} of 5.1.

Table 4.1 Estimates for the toxicity of D5 generated from log K_{ow} 6.49 and log K_{ow} of 5.1

	Toxicity test	Log K_{ow} 6.49 (mg/l)	log K_{ow} 5.1 (mg/l)
Fish	96 hour LC_{50}	0.037	0.56
	28–32 day NOEC	2.1×10^{-3}	0.038
Daphnids	48 hour LC_{50}	9.7×10^{-3}	0.20
	16 day EC_{50}	6.4×10^{-4}	0.019
Green algae	72–96 hour EC_{50}	5.7×10^{-3}	0.14

The equations in the TGD are applicable to chemicals that act by non-polar narcosis and are well validated. The relevant validation statistics [*n* is the number of chemicals used to derive the quantitative structure–activity relationships (QSARs) equation, R^2 is the correlation coefficient (coefficient of determination), Q^2 is the cross-validated correlation coefficient, and s.e. is the standard error of estimate] are:

- fish, 96 hour LC50 = –0.85 × log Kow – 1.39 mol l–1 (n = 58, R2 = 0.94, Q2 = 0.93, s.e. = 0.36);
- fish, 28–32 day log NOEC = –0.90 × log Kow – 2.30 mol l–1 (n = 27, R2 = 0.92, Q2 = 0.91, s.e. = 0.33);
- daphnids, 48h log EC50 = –0.95 × log Kow – 1.32 mol l–1 (n = 49, R2 = 0.95, Q2 = 0.94, s.e. = 0.34);
- daphnids, 16 day log NOEC = –1.05 × log Kow – 1.85 mol l–1 (n = 10, R2 = 0.97, Q2 = 0.95, s.e. = 0.39);
- green algae 72–96 hour log EC50 = –1.00 × log Kow – 1.23 mol l–1 (n = 10, R2 = 0.93, Q2 = not determined, s.e. = 0.17).

The range of log K_{ow} values to which the equations apply are not given in the TGD and so the relevance of these estimates to a substance with a log K_{ow} of 6.49 cannot be established.

The toxicity of D4 to aquatic organisms is also estimated using the USEPA EPI (v3.12) software, which estimates the toxicity from the log K_{ow} value using various QSARs. A log K_{ow} of 5.09 (as estimated by the software) is used in the estimates, as the equations were developed using calculated log K_{ow} values. (The QSARs for neutral organics are used in the estimates – these are reported to apply to non-reactive, non-ionisable compounds, such as alcohols, ketones, ethers, alkyl halides, aryl halides, aromatic hydrocarbons, halogenated aromatic and aliphatic hydrocarbons, and sulfides and disulfides). The results obtained are given in Table 4.2.

Table 4.2 Estimates for the toxicity of D5 generated from log K_{ow} 5.09 using USEPA EPI (v3.12) software

	Toxicity test	**log K_{ow} = 5.09 (mg/l)**
Fish	96 hour LC_{50}	0.27 (freshwater)
	96 hour LC_{50}	0.28 (saltwater)
	14day LC_{50}	0.81
	30 day Chv	0.058
Daphnids	48 hour LC_{50}	0.072
	16 day EC_{50}	0.014
Mysid shrimp	96 hour LC_{50}	0.009
Green algae	96 hour EC_{50}	0.27
	96 hour Chv	0.16

Note [1]Chronic value, which most probably represents the geometric mean of the lowest observed concentration (LOEC) and the NOEC.

The relevant validation statistics for the EPI (v3.12) methods are:

- fish, 96 hour log LC50 (freshwater) = –0.94 × log Kow + 1.75 mmol/l (n = 60, R2 = 0.94, applicable to log Kow up to 5.0);
- fish, 96 hour log LC50 (saltwater) = –0.73 × log Kow + 0.69 mmol/l (n = 37, R2 = 0.66, applicable to log Kow up to 5.0);
- fish, 14 day log LC50 = –0.871 × log Kow + 1.87 mmol/l (n = 50, R2 = 0.98, applicable to log Kow up to 8.0);
- fish, 30 day log Chv = –0.87 × log Kow + 0.72 mmol/l (n = 20, R2 = 0.91, applicable to log Kow up to 8.0);
- daphnids, 48 hour log LC50 = –0.91 × log Kow + 1.72 mmol/l (n = 19, R2 = 0.99, applicable to log Kow up to 5.0);
- daphnids, 16 log day EC50 = –0.72 × log Kow + 0.05 mmol/l (n = 5, R2 = 0.99, applicable to log Kow up to 8.0);
- mysid shrimp, 96 hour log LC50 = –1.25 × log Kow + 1.83 mmol/l (n = 17, R2 = 0.71, applicable to log Kow up to 5.0);
- green algae, 96 hour log EC50 = –0.885 × log Kow + 1.466 mmol/l (n = 7, R2 = 0.91, applicable to log Kow up to 6.4;
- green algae, 96 hour log Chv = –0.634 × log Kow – 0.036 (n = 7, R2 = 0.99, applicable to log Kow up to 8.0).

The water solubility of D4 is around 0.056 mg/l and so these predicted acute toxicity values are above its water solubility, except for Mysid shrimp. The predictions for Mysid shrimp are generally not consistent with those obtained for fish, daphnids, and algae, and are not consistent with the available toxicity data for Mysids, and so the reliability of this estimate is uncertain.[21] Overall the available estimates for toxicity suggest that D4 is not toxic to aquatic organisms at concentrations up to its water solubility over short-term exposures, but

[21]Details of the chemicals included in the training set for the Mysid shrimp QSAR are given in Clements *et al.* (1988). As well as neutral organics, it appears that several pesticides, including an organophosphorous insecticides (leptophos) and a pyrethroid insecticide (fenvalerate) are included in the chemicals used to construct this QSAR. This, therefore, casts further doubt on the applicability of this QSAR to D4.

may be toxic at concentrations below its water solubility on longer exposure. This is a similar pattern to that shown by the available experimental data.

Of particular importance for D4 are the predictions for the toxicity to algae, as no valid test data are available for these. The above estimates show that both the method given in the TGD and the EPI (v3.12) software lead to values for the estimated 72–96 hour EC_{50} of 5.7×10^{-3} to 0.14 mg/l and 0.27 mg/l, respectively. Most important to the predicted no-effect concentration (PNEC) derivation is the algal NOEC (Chv) value. An estimate for this is only available using the EPI (v3.12) software (96 hour Chv = 0.16 mg/l). The QSAR used in the EPI (v3.12) software for this endpoint was derived from data on seven substances (polyether, isolinalool, *trans*-anethole, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and hexachlorobenzene) that cover a log K_{ow} range of 1.9–6.4. The R^2 value for the QSAR equation is 0.99. Therefore, although the number of chemicals used to develop this QSAR is relatively small (seven in total), there is no reason to suspect that it is not applicable to D4. In addition, the estimated Chv of 0.16 mg/l is reasonably consistent with some of the estimated algal EC_{50} values for D4. However, an estimated EC_{50} for alga is considerably below this value ($EC_{50} = 5.7 \times 10^{-3}$ mg/l) and so there is some uncertainty in this value.

4.1.5 Overall summary of standard endpoint toxicity data

Overall, D4 is not toxic to fish and invertebrates when they are exposed for short durations (e.g. up to 96 hours) at concentrations up to the water solubility limit of D4. On longer exposure, toxicity to both fish and invertebrates (daphnids) is apparent and the calculated long-term NOECs are 7.9 µg/l for *D. magna* based on survival and ≥4.4 µg/l for *O. mykiss* based on survival, embryo viability, and growth.

The results of toxicity tests with algae are not considered valid for use in risk assessment. Although there is some uncertainty over the actual algal NOEC, the available QSAR estimates for algae suggest that algae should not be significantly more sensitive to D4 than fish and invertebrates.

4.1.6 Endocrine disruption

No data are available for investigations into the effects of D4 on the endocrine system in aquatic organisms.

4.1.7 Wastewater treatment plant micro-organisms

IUCLID (2005) reports a 3 hour EC_{50} of >10,000 mg/l for D4 in an unpublished ISO 8192 test for inhibition of oxygen consumption by activated sludge.

Kim *et al.* (2006) investigated the toxicity of D4 to a gram-negative bacterium (*Escherichia coli*) and a gram-positive bacterium (*Staphylococcus aureus*). The tests were carried out by adding D4 to an aqueous solution of each bacterium (between 2×10^8 and 6×10^8 colony-forming units/ml). The solution was mixed for one hour by stirring and the samples then diluted using phosphate-buffered saline and plated on plate-count agar. The plates were incubated at 37°C for 24 hours and the number of colonies counted. D4 showed little or no toxicity (reduction in number of viable bacteria) compared to the controls at concentrations as high as 10 per cent (0.1 g/g solution).

Michalke *et al*. (2006) found that D4 stimulates the methylation of bismuth to trimethylbismuth by *Methanosarcina barkeri* and *Desulfovibrio vulgaris*. The stimulatory effect is not thought to be specific to D4, but membrane permeation of the metal ion is thought to facilitate the effect. The environmental significance of these findings, in terms of the risk assessment for D4, is unclear.

4.1.8 Toxicity to sediment organisms

Kent *et al*. (1994) and Springborn Laboratories (1991a, 1991b) investigated the toxicity of D4 to *C. tentans* in water-only exposure and sediment exposure. The results from the water-only experiments are summarised in Section 4.1.2.

The D4 tested (purity 99 per cent) was mixed with ^{14}C-D4. Three sediments were used in the study, with organic carbon contents of 0.27, 2.3, and 4.1 per cent, respectively. The sediments used were mixtures of different ratios of pond sediment, sand, and dried compost (cow manure). The sediments were sterilised prior to use. The dilution water used in the study was well water of hardness 20–40 mg/l as $CaCO_3$ and a pH of 6.9–7.5.

D4was added to the dried sediment as a solution in acetone and then the sediment was thoroughly mixed and allowed to stand overnight to allow the acetone to evaporate. Five test concentrations (nominally 50, 100, 200, 400, and 800 mg/kg dry weight) were tested for each sediment type. A control and solvent control sediment were also prepared in the same way, but without D4. To prepare test sediments (in duplicate) the spiked sediment was added to the test vessel (of volume 3.8 l) to a depth of 5 cm and the test vessel filled with dilution water. The tests were carried out using a continuous flow of water through the vessel. Test vessels with sediments of low and middle organic carbon content had no headspace to prevent loss of D4 through volatilisation. However, for experiments with sediments of high organic carbon content, the test vessels were not sealed because it was difficult to maintain the dissolved oxygen content with the sealed system. The test was started by adding 50 midges (second instar larvae) per treatment to the test vessels (the flow of water was stopped for 24 hours to allow the midges time to initiate tube construction). During the test the larvae were fed flaked fish-food suspension daily. The organisms were exposed to D4 for 14 days.

The endpoints determined in the study were survival and growth (wet weight) of the midge larvae. The normal life cycle of the test species includes a progression through several benthic instar stages followed by a pupae stage at which the developing larvae float to the water surface and obtain their oxygen requirements directly from air. However, for the tests in which there was no headspace once the organisms reached this stage they suffocated. Therefore the criteria used to assess survival were modified to take this into account (i.e. the dead organisms in the pupae or adult stage were taken as positive indicators of organism survival at the stages up to this point). Only the organisms found dead in the larval stages or missing at test termination were considered dead.

During the test, samples of the sediment, overlying water, and interstitial water were collected on days 0, 3, 7, 10, and 14 and analysed for D4 concentration. The mean measured concentrations in the sediments were around:

- 16 per cent of the nominal in those of low organic carbon (actual concentrations 6.8, 17, 32, 65, and 130 mg/kg dry weight for the nominal 50, 100, 200, 400, and 800 mg/kg dry weight treatment groups, respectively);
- 35 per cent of nominal in those of middle organic carbon (actual concentrations were 18, 38, 76, 120, and 250 mg/kg dry weight for the nominal 50, 100, 200, 400, and 800 mg/kg dry weight treatment groups, respectively);

- 26 per cent of nominal in those of high organic carbon (actual concentrations 2.6, 7.4, 19, 54, and 170 mg/kg dry weight for the nominal 50, 100, 200, 400, and 800 mg/kg dry weight treatment groups, respectively).

The loss of D4 (compared to the nominal values) is thought to have occurred mainly during the test sediment preparation prior to addition of the dilution water. The levels of D4 in the overlying water were generally below the detection limit

(<ca. 0.05 mg/l) in the experiments with sediment of low and middle organic carbon. For the sediment of high organic carbon content, the concentration of D4 in the overlying water was generally below the detection limit (the detection limit for these samples was 0.007 mg/l) at the three lowest exposure concentrations, but for the two sediments of highest exposure the mean concentrations were 0.036 mg/l and 0.054 mg/l, respectively. The measured levels of D4 in the interstitial water are considerably higher than the water solubility of the substance (e.g. the interstitial water concentrations were 0.76–3.6 mg/l in the sediments of low organic carbon, 0.17–0.87 mg/l in those of middle organic carbon, and 0.019–1.1 mg/l in those of high organic carbon), which possibly reflects both dissolved and particulate-bound D4 in the samples. Therefore the interstitial water samples are thought not to give a true indication of the actual exposure concentration from the porewater alone.

Statistically significant (p = 0.05) effects were seen on mean larval wet weight at the highest concentration tested in the sediments of low organic carbon and statistically significant effects were seen on survival at the highest concentration tested in those of middle and high organic carbon. However, that the control survival was only 69 per cent in the sediments of middle organic carbon and so this result is not considered valid.

The overall 14 day NOECs from this study are 65 mg/kg dry weight in the sediments of low organic carbon and 54 mg/kg dry weight in those of high organic carbon. The results from this study are summarised in Table B 8 in Appendix B.

The same results are reported in Walker (1993). However, this paper also indicates that an initial study was carried out with a sediment of high organic carbon (3.9 per cent) and the same system as described above [this study is also reported in Springborn Laboratories (1991a)]. This study shows statistically significant (p = 0.05) mortality at all concentrations tested [survival was 21–26 per cent at measured D4 sediment concentrations of 16, 32, 59, 110, and 200 mg/kg dry weight, compared to control survival of 74 per cent (control), 72 per cent (solvent control), and 73 per cent (pooled control)]. No explanation is given for the differences between results of the test with 3.9 per cent organic carbon and those from the test with 4.1 per cent organic carbon, but it is clear from the data reported in Walker (1993) that the control survival was relatively poor (<80 per cent) in the study with 3.9 per cent organic carbon content and so the result is not considered valid for use in this risk assessment.

Maycock *et al.* (2005) raise a number of other concerns in relation to these studies, in particular:

- It appears only a short time was allowed for D4 to equilibrate between the sediment and water prior to addition of the test organisms (around 24 hours, although this is not explicitly stated in the test report).
- The use of only two replicates per treatment (the current OECD test guideline for this species recommends a minimum of three replicates) and the relatively large intervals between test concentrations mean that the statistical power of the test to detect true differences in toxic response may not be optimal.
- Growth was determined based on the mean wet weight of the surviving larvae. The OECD method recommends using ash-free dry weight of organisms as a

measure of growth, as the grain size of sediments influences the amount of sediment that Chironomus spp. ingest and retain in their gut (and hence the wet weight of the organism). Use of wet weight means that the reliability of the test in interpreting differences, or lack of them, in growth as a true reflection of toxic response is reduced.

- The assumption that deaths of the pupae and adults found in the study are not treatment-related (i.e. were included in the survival figures) may not be appropriate. For example, the normal behaviour of C. tentans is that the pupae leave the larval tubes after the larval-pupa moult and then swim on the surface. However, such pupae continue to rely on dissolved oxygen in the water column at this time (rather than breathe air directly). This pupal stage lasts about three days. After this the pupa then rise to the surface of the water column just prior to eclosion. The emergence process then takes about 15 seconds. Thus, it is possible that some pupal mortalities were caused by toxic effects of the chemical rather than suffocation as assumed in the test report.

Also, this test was carried out with supplemental feeding (and so the food added was not contaminated with D4). The TGD now recommends that sediment toxicity tests should be carried out, wherever possible, without supplemental feeding. The effect of the supplemental feeding on the result of the study is unknown.

Overall, despite the limitations with the available studies, for a volatile substance such as D4 the tests were the best technically achievable at the time , and so the results from the tests carried out with the sediments of low and high carbon reported in Kent *et al.* (1994) should be considered in relation to the PNEC derivation. The lowest NOEC from these tests was the 14 day NOEC of 54 mg/kg dry weight for the high carbon sediment.

Krueger *et al.* (2008) recently completed a repeat study using *C. riparius* and D4 of purity 99.75 per cent. An artificial sediment was used (based on the recommendations in OECD test guideline 218) that consisted of 10 per cent sphagnum peat moss, 20 per cent silt and clay, and 70 per cent industrial quartz sand. The organic carbon content and pH of the sediment used were 4.1 per cent and 6.9, respectively. D4 was added to the sediment in a two-stage process. Firstly, neat test material was added to air-dried peat and mixed overnight. Secondly, the formulated sediment was added to the peat and mixed for 20 minutes. A 28-day ration of food was mixed into the sediment prior to addition of the water (well water was used). The test vessels used were 2 l glass beakers that contained a 2 cm depth of sediment and an 8 cm depth of overlying water.

The nominal test concentrations prepared were 31, 63, 125, 250, 500, and 1000 mg/kg dry weight plus a control and eight replicates were prepared – four to evaluate the biological endpoints, three to confirm analytically the sediment concentrations on days 0, 7, and 28, and one for water-quality measurements on day 0. Further water-quality measurements were taken from the replicates during the test. The sediments were allowed to equilibrate for 48 hours prior to addition of the test organism. At test initiation 20 midges per replicate were introduced (80 midges per treatment) and the sediments were incubated at 20°C for 28 days. During the incubation the test chambers were covered with loose-fitting lids and the water phase continuously aerated (the aeration rate was such as to avoid disturbance of the sediment).

The concentration of D4 in the sediment phase was determined on day 0, day 7, and day 28 of the test. The mean measured concentrations were < LOQ, <LOQ, 19, 44, 131, and 355 mg/kg dry weight for the nominal 31, 63, 125, 250, 500, and 1000 mg/kg dry weight treatment groups, respectively. The measured concentrations are therefore much lower than the nominal concentrations (range 15–36 per cent of nominal), which most probably reflects mainly the loss during sediment preparation. In addition, the measured data, in some cases, show a general decreasing concentration with time (although, as Table 4.1

shows, there is some variation in the data), which indicates that some loss from the test system could have occurred during the test (possibly through aeration of the water phase or hydrolysis).

During the test the dissolved oxygen concentration in the water phase was ≥7.2 mg/l, the pH was between 8.2 and 8.6, and the hardness was 140–154 mg/l as $CaCO_3$. The level of ammonia in the water phase, monitored at weekly intervals during the test, was above 4 mg/l on days 7, 14, and 21 (generally similar levels were present in the control and treatment groups). As a result, the overlying water was partially replaced on these days to minimise potential toxicity from ammonia.

The biological results are summarised in Table 4.3.

Table 4.3 Effects of D4 on *Chironomus riparius* (Krueger *et al.*, 2008)

Measured exposure concentration (mg/kg dry weight)				Biological endpoints (at 28 days)			
Day 0	**Day 7**	**Day 28**	**Mean**	**Mortality (%)**	**Mean development time (days)**	**Mean emergence ratios**	**Mean development rate**
<13	<12	<14	6.5 [1]	13	17.5	0.88	0.0597
<18	<15	<15	7.9 [1]	11	17.9	0.89	0.0584
21	27	<16	19	2.5	17.9	0.98	0.0586
47	50	36	44	19	18.7	0.85	0.0560
120	170	101	131	55 [2]	18.0	0.48 [2]	0.0579
450	360	255	355	88	21.1 [2]	0.13*	0.0496 [2]
Control				8.8	18.4	0.93	0.0572

Notes: [1]The mean was estimated assuming the actual concentration was the LOQ divided by two.
[2]Statistically significant difference (p = 0.05) from control.

Emergence first occurred on day 15 of the test. A dose-related increase in mortality at 28 days (which included organisms that died in the pupal and larval stages, that emerged and died, and that did not emerge by day 28) was evident in the test and the 28 day LC_{50} was 114 mg/kg dry weight (95 per cent confidence limits of 96 and 136 mg/kg dry weight).

The LOECs and NOECs for the other endpoints studied (development time, emergence ratio, and development rate) were (all for 28 days):

- NOEC mortality, 44 mg/kg dry weight
- LC50 mortality, 114 mg/kg dry weight
- NOEC development time, 131 mg/kg dry weight
- LOEC development time, 355 mg/kg dry weight
- NOEC emergence ratio, 44 mg/kg dry weight
- LOEC emergence ratio, 131 mg/kg dry weight

- NOEC development rate, 131 mg/kg dry weight
- LOEC development rate, 355 mg/kg dry weight

Overall, the NOEC from this study was 44 mg/kg dry weight based on development rate, which is based on the mean measured concentration during the test. As

Table 4.3 shows, there is some variation in the levels measured during the test and, at the lower concentrations tested, the level of D4 is below the LOQ. However, at the treatment levels at or around the NOEC and LOEC, D4 could be determined at all time points and so the results are considered to be reliable. In addition, the results generally confirm those from the earlier study by Kent *et al*. (1994) with *C. tentans*. However, as the Krueger *et al.* (2008) study was carried out without supplemental feeding and considers survival after 28 days rather than 14 days, and (as discussed above) there may be further limitations with the Kent *et al*. (1994) study, the results from Krueger *et al.* (2008) are considered in the PNEC derivation in preference to those of Kent *et al*. (1994).

4.1.9 Predicted no-effect concentration for the aquatic compartment

4.1.9.1 Surface water

The lowest long-term NOEC is ≥4.4 µg/l from a long-term (93 day) fish toxicity study with *O. mykiss* (this was the highest concentration tested in this study). In addition, a 14 day toxicity study with the same species gave an NOEC of 4.4 µg/l. Normally the results of a 14 day study are treated as an acute toxicity result for the PNEC derivation, but in this case the result is consistent with the limit NOEC from the long-term toxicity study and so the overall NOEC for D4 used is 4.4 µg/l, which takes into account both test results. As long-term NOEC data are available for fish and *Daphnia* an AFof 50 should be applied to this result. However, QSAR estimates suggest that algae are not more sensitive than invertebrates and, in addition, the fish NOEC is actually a limit value from a study in which no effects were seen. Therefore, in this case an AF of ten is applied to the lowest NOEC in this case, and so the PNEC for surface water is 0.44 µg/l.[22]

For the PNEC for marine organisms, an AF of 100 is applied to the fish NOEC. This gives a PNEC for the marine environment of 0.044 µg/l.

4.1.9.2 Microorganisms

An EC_{50} of >10,000 mg/l was determined for D4 in an activated sludge respiration inhibition test. A PNEC for wastewater treatment microorganisms of >100 mg/l can be derived from this value using an AF of 100.

4.1.9.3 Sediment

A NOEC of 44 mg/kg dry weight was obtained for D4 in a 28 day study with *C. riparius.* The sediment used in this study had an organic carbon content of 4.1 per cent. When

[22]This is based on a test in which no effects were seen. If the *Daphnia* NOEC is used, the PNEC is 0.79 µg/l.

normalising to a standard organic carbon content of 5 per cent (as recommended in the TGD) this value gives a $NOEC_{standard}$ of 54 mg/kg dry weight.

According to the TGD an AF of 100[23] is applied to the result from a long-term toxicity test for a single species of sediment organism. This gives a $PNEC_{sediment}$ of 0.54 mg/kg dry weight or 0.11 mg/kg wet weight [as calculated by EUSES using the default water content of sediment given in the TGD (around 79 per cent by weight)]. The equivalent PNEC for sediment derived using the equilibrium partitioning method is 0.16 mg/kg wet wt.

The PNEC of 0.12 mg/kg wet weight derived from the available sediment toxicity data is used in the risk assessment.

For the marine assessment, the appropriate AF for the available data is 1000. This gives a $PNEC_{marine\ sediment}$ of 0.054 mg/kg dry weight or 0.012 mg/kg wet weight.

4.2 Terrestrial compartment

4.2.1 Terrestrial toxicity data

A 14 day LC_{50} of 204 mg/kg dry soil for earthworms can be estimated for D4 using the USEPA EPI (v3.12) estimation software and a log K_{ow} of 5.09 similar to the predictions for aquatic toxicity a predicted log K_{ow} of 5.09 is used in the estimates as the equation was developed mainly with predicted rather than measured log K_{ow} values). This software estimates the toxicity from the log K_{ow} value using a QSAR for neutral organics. The QSAR used in the software:

$$\log 14\ \text{day}\ LC_{50} = 1.405 - 0.308 \times \log K_{ow} \qquad (4.1)$$

where LC_{50} is estimated in units of mmol/kg dry soil.

The QSAR was developed using experimental data from Neuhauser *et al.* (1985, 1986) and appears to be based on five data points only. The coefficient of determination of the method (R^2) is 0.48.

The method is reported as valid for log K_{ow} up to 5.0. The log K_{ow} value used in the calculation for D4 is 5.09, but the actual log K_{ow} for D4 may be considerably higher than this (log K_{ow} of 6.49). According to the help files within EPI (v3.12) one of the limitations of the method for substances with log K_{ow} >5.0 is that a test duration longer than 14 days may be needed for these to express their toxicity.

Details of the chemicals used to derive the QSAR are not given within the EPI (v3.12) program. However, further details of the method are given in Clements *et al.* (1988).[24] According to this report the five chemicals included in the training set used to derive the QSAR are 2-chlorovinyl ether, nitrobenzene, 1,2-dichloropropane, fluorine, and 1,2,4-trichlorobenzene. The range of log K_{ow} values covered by the training set is from 1.0 to 4.3.

[23] Recent data for the related substance D5 indicate that a second species (*Lumbriculus variegatus*) is less sensitive to D5 than *Chironomus* spp. (Environment Agency, 2008a). If the same relative sensitivity of species is assumed for D4, then this reduces the assessment factor from 100 to 50, which has no effect on the overall conclusions of the assessment for sediment.

[24] In Clements *et al.* (1988) the same QSAR equation is given, but the units of the predicted LC_{50} are stated to be mmol/l rather than mmol/kg dry soil. It is assumed here that the correct units were incorporated into the EPI (v3.12) software.

Given that the QSAR was derived using only a limited number of chemicals (five), the relatively poor R^2 value for and the unknown applicability of the method to D4, the LC_{50} estimated using this method is considered uncertain. However, few other QSAR methods to estimate the toxicity of chemicals such as D4 to terrestrial organisms are currently available.

4.2.2 PNEC for the soil compartment

According to the TGD, in the absence of actual toxicity data for terrestrial organisms, the PNEC for soil can be estimated using the equilibrium partitioning method. Using the PNEC for water of 0.44 µg/l, the PNEC for soil is estimated as 0.16 mg/kg wet weight with this approach.

Using the QSAR value for toxicity to earthworms, an indicative value is estimated as 0.20 mg/kg dry weight using an AF of 1000. This value is equivalent to a value of 0.18 mg/kg on a wet weight basis, which is in good agreement with the PNEC derived by the equilibrium partitioning method. However, the reliability of this indicative value is unclear and so the PNEC based on the equilibrium partitioning method is considered in the risk assessment.

The PNEC for soil is taken as 0.16 mg/kg wet weight (as derived by the equilibrium partitioning method) for the risk assessment. As the log K_{ow} value for D4 is >5, the risk characterisation ratios that result are increased by a factor of ten, in line with the recommendations in the TGD.

4.3 Atmospheric compartment

4.3.1 Toxicity data relevant to the atmospheric compartment

No toxicity data are available for the atmosphere.

D4 is very volatile and reacts readily with hydroxyl radicals in the atmosphere. Therefore the potential for D4 to contribute to the formation of low-level photochemical smog needs to be considered. Chandra (1997) carried out a series of experiments with D4 in simplified model photochemical smog chambers. The experiments consisted of repeated six hour irradiations of a standard mixture of photochemical smog precursors with various amounts of D4. D4 strongly inhibited the formation of ozone in these experiments. Furthermore, airshed model simulations to represent 39 different urban areas in the USA, and also a trajectory model to simulate a pollution episode in Europe, predicted that D4 inhibits ozone formation. Although it is recognised that the overall mechanism for photochemical smog formation is very complicated, and depends on numerous variables (and so it is impractical to address all of these in laboratory simulations), it appears that D4 does not contribute significantly to (indeed, appears to inhibit) the low-level formation of atmospheric ozone during photochemical smog episodes.

As the main products of the atmospheric degradation of D4 appear to be hydroxylated (see Section 0), which have lower vapour pressures than D4 itself, it is possible that if these products are not removed rapidly from the atmosphere by wet or dry deposition, they could condense onto aerosol particles already in the atmosphere. Chandra (1997) reports the results of a series of screening experiments to investigate the potential for D4 to contribute to aerosol formation in the atmosphere using a similar photochemical smog chamber. Aerosol formation does not enhance observed when D4 is added to the chambers at concentrations of ~0.1–0.9 ppm_V. Therefore, based on these results, it is unlikely that the

degradation products from D4 contribute significantly to atmospheric aerosol formation (although, of course, atmospheric aerosol formation depends on many factors and it is impractical to investigate all these factors in a laboratory setting).

4.3.2 PNEC for the atmospheric compartment

As no toxicity data are available it is not possible to derive a PNEC for the atmospheric compartment.

4.4 Mammalian toxicity

4.4.1 Toxicokinetics

D4 toxicokinetic data by inhalation and dermal routes are available for humans, and for rats by all relevant routes of. The available evidence suggests that the toxicokinetic behaviour of D4 in humans is qualitatively similar to that in the rat.

Mass-balance studies in animals show that around 4–8 per cent of the inhaled concentration of D4 is absorbed (Dow Corning, 1996a, 1996b, 1997a). In human volunteers around 6–17 per cent of the inhaled concentration was absorbed (Utell *et al.*, 1998; Dow Corning, 2000d). In rats around 52 per cent of an oral dose given in corn oil is absorbed (Dow Corning, 1998). In rats and humans, 0.5–1 per cent of the applied dose of D4 is absorbed across the skin, and the extent of absorption is limited by evaporation (Dow Corning, 2000a, 2000b). Absorbed D4 is distributed widely throughout the body and preferentially locates in fat as parent D4 (Huntingdon Research Centre, 1995; Dow Corning, 1996b, 1997a). However, the potential for bioaccumulation in rats through enzyme induction and enhancement of excretion is likely to be limited. Possible differences in distribution may arise when D4 is given orally compared to the inhalation route. Pharmacokinetic modelling work cited in CES (2004) suggests that when D4 is given orally, it is absorbed in the form of chylomicrons via the lymphatic system. Chylomicrons are removed from the bloodstream and broken down by the reticuloendothelial system in the liver,and hence a lower proportion of the absorbed dose may be available for systemic distribution compared to that from inhalation exposure.

A proportion of D4 is metabolised with the two major metabolites dimethylsilanediol and methylsilanetriol (Dow Corning, 1997b). Some evidence suggests that the F344 rat may metabolise D4 more readily than the Sprague Dawley rat, but it is unclear what impact this has on the toxicity of D4 in these strains of rat (Dow Corning, 2000c). Also, studies using rats, hamsters, rabbits, guinea pigs, and mice show evidence for species differences in D4 metabolism. Hamsters, mice, and (to a lesser extent) rats preferentially metabolise D4 to methylsilanetriol, which appears to be responsible for liver enzyme induction and liver weight increases (Dow Corning, 2001).

The main routes of elimination for absorbed D4 and/or its metabolites are in the urine and exhaled air, with the faeces a minor route.

4.4.2 Acute toxicity

Information on the effects of single inhalation and dermal exposure on humans is available from kinetics studies. Single-exposure studies in animals are available for all relevant routes.

Utell *et al.* (1998) report no adverse effects on human volunteers exposed to 10 ppm D4 for one hour. Dow Corning (2000e) reports no adverse effects on volunteers administered a 24-hour non-occlusive dermal application of 1 or 1.4 g to the underarms.

The LC_{50} for a single inhalation exposure of four hours in the rat is 36 mg/l (RCC, 1994). RCC (1994) reports transient body-weight loss, but no mortality, at the lowest tested concentration (20 mg/l) in this study. In an earlier study, the only finding in rats that inhaled 12 mg/l for four hours was mild non-specific signs of toxicity during exposure (Pauluhn, 1984). Löser (1979) did not observe any overt signs of toxicity in rats given 4800 mg/kg by the oral route, as was the case for rats given 2400 mg/kg by the dermal route (Ramm, 1985).

4.4.3 Irritation

D4 is not a skin irritant in humans and is not a skin or eye irritant in animals (Bayer, 1979, 1988, 1999; Dow Corning, 2000e). In human volunteers who inhaled 10 ppm D4 for one hour there was no evidence of sensory respiratory irritation (Utell *et al.*, 1998).

4.4.4 Sensitisation

A maximisation test in guinea pigs for the sensitising potential of D4 gave negative results (Bayer, 1985). There is no information on the potential asthmagenicity of D4. However, D4 has no skin-sensitising properties and, based on what is generally known for this class of compound, it is not predicted to show asthmagenic potential.

4.4.5 Repeated dose toxicity

No information about the effects on humans of repeated exposure to D4 is available. Repeated exposure studies in animals are available for all relevant routes of exposure.

4.4.5.1 Inhalation

Several inhalation studies are available for rats exposed for periods that ranged from 14 days to two years. In general, the results consistently show that the main target sites for the effects of D4 are the liver and the respiratory tract.

Site of contact effects in the respiratory tract

The effects on the respiratory tract comprise nasal rhinitis and pulmonary inflammation. A two year inhalation study for nasal and lung effects in F344 rats (Battelle Toxicology Northwest, 2004) gives a no observed adverse effect level (NOAEL) of 30 ppm. At the next highest exposure of 150 ppm, an increased incidence of eosinophilic globules in the nasal epithelium indicates a mild rhinitis response. The highest exposure of 700 ppm leads to severe rhinitis.

Systemic effects

The main systemic effect observed after repeated inhalation exposure to D4 is a dose-related increase in liver weight and associated hypertrophy. Increases in liver weight greater than 10 per cent are considered outside the range of natural variation and therefore adverse. In general, liver weight increases >10 per cent, which were observed with a concentration as low as 10 ppm, are not accompanied by any consistent evidence of biochemical changes that indicate impaired liver function. In some studies with concentrations of 500 ppm and above, the liver weight changes are accompanied by an increased incidence of hepatocyte hypertrophy (RCC, 1995a; Stump *et al.*, 2001). Inhalation studies with D4 also reveal increases in adrenal gland weights and decreases in thymus and ovary weights, but only at high concentrations (Dow Corning, 1989; RCC, 1995a, 1995b; Stump *et al.*, 2001).

There is evidence that the magnitude of the effects of D4 on the liver differ between species. In a multi-species study, Sprague Dawley rats, CD-1 mice, Golden Syrian hamsters, New Zealand white rabbits, and Hartley guinea pigs were exposed to 700 ppm (8470 mg/m^3) D4 for six hours per day for five days per week over five weeks (Dow Corning, 1999). Mice were the most sensitive species to liver enlargement, with the largest liver weight gains of 60–80 per cent. Hamsters and rats also showed liver weight gains, but lower at 20–40 per cent. No effects on liver weights are reported for guinea pigs or rabbits. The increases in liver weights correlate with the amount of the methylsilanetriol metabolite detectable in the urine.

Liver weight increases involve transient hyperplasia followed by sustained hypertrophy, which is caused by the induction of hepatic enzymes with a similar profile to those seen in phenobarbital-treated rats (Dow Corning, 1996c, 1996d; McKim *et al.*, 2001). A comparison of enzyme induction in rats and guinea pigs in the above multi-species study demonstrates clear evidence for induction in rats with no induction of microsomal enzymes in guinea pigs (Dow Corning, 1999). Enzyme induction was not assessed in other species.

In a 28 day study, F344 rats were exposed to D4, six hours per day for five days per week at 226, 417, 700, or 1154 ppm (RCC, 1995a). Four in ten females died at 1154 ppm before day six and therefore exposure was lowered to 1076 ppm for the remainder of the study. Toxicologically significant liver weight increases occurred from 417 ppm. At 417, 700, and 1154 ppm liver weights increased above controls by 16, 21, and 26 per cent, respectively, in males, and by 19, 33, and 43 per cent in females, respectively. While increases in liver weight were observed in both males and females, females appeared more sensitive to this effect with increases nearly double those in males. Hepatocellular hypertrophy occurred in five in ten males and four in ten females at 700 ppm, and in seven in ten males and four in ten females at 1154 ppm. This study for liver enlargement gives NOAEL of 226 ppm.

Data are available from three 90 day inhalation toxicity studies (two in Sprague Dawley rats and one in F344 rats). During the 90 days Sprague Dawley rats received D4 vapour by whole-body exposure for six hours per day for five days per week at 0, 5, 10, or 300 ppm (Global Silicon Producer Association, 1991). In each study, treatment was followed by a four week recovery period for some high-dose groups and controls. The increases in liver weights were toxicologically significant in females only (compared to controls, by 11, 14, and 28 per cent at 5, 10, and 300 ppm, respectively). In a second study, Sprague Dawley rats were exposed for 7 days per week at 50, 300, or 700 ppm (Dow Corning, 1989). Liver weights at 50, 300, and 700 ppm increased above controls by 24, 17, and 27 per cent in males, and by 0, 10, and 20 per cent in females, respectively. In both studies, in top-dose animals allowed a four week exposure-free period, liver weight increases almost completely reversed (<5 per cent) and there were no histopathological changes. The NOAEL for liver weight increase in Sprague Dawley rats after inhalation exposure to D4 for 90 days was 5 ppm based on a 14 per cent increase in liver weight at 10 ppm.

F344 rats were treated for six hours per day for five days per week to over 90 days with D4 vapour by nose only at exposures of 35, 122, 488, or 898 ppm (RCC, 1995b). At 898 ppm, five of the 30 females died. No increases in liver weight of 10 per cent or more above those of controls were observed in males. Liver weights in females were 20 and 25 per cent greater than those of controls at 488 and 898 ppm, respectively. No histopathological changes of the liver occurred in any of the treated groups. In top-dose recovery animals, liver weights were similar to those of controls (within 5 per cent). In this study the NOAEL was 122 ppm based on a 20 per cent increase in female liver weights at 488 ppm.

In a two year rat bioassay, groups of 96 F344 rats were exposed to 0, 10, 30, 150, or 700 ppm D4 for six hours per day for five days per week for up to 24 months (Battelle Toxicology Northwest, 2004). Rats were sacrificed after six months (six males, six females), 12 months (ten males, ten females), or 24 months (60 males, 60 females. An additional group of rats (20 males, 20 females) were exposed to D4 for 12 months only and sacrificed at 24 months. At six months, liver weight increased by ≤10, 16, 14, and 27 per cent in males, and ≤10, ≤10, 10, and 20 per cent in females at 0, 10, 30, 150, and 700 ppm, respectively. At 12 months, liver weight increased by ≤10, 12, 16, and 32 per cent in males, and ≤10, ≤10, 14, and 29 per cent in females, respectively. In males treated with 700 ppm, increased liver weights were also accompanied by centrilobular hepatocyte hypertrophy in 60 per cent of the animals. At 24 months, liver weight increased in males only at 700 ppm (27 per cent), in females at 150 ppm and 700 ppm (by 14 and 30 per cent, respectively). Liver weight increase in 8 per cent of the top-dose males was also accompanied by centrilobular hepatocyte hypertrophy. There is evidence that liver weight increase was fully reversible in females, but not males. In males exposed for 12 months and allowed a 12 month exposure-free recovery, liver weights increased by 10, 13, and 22 per cent at 30, 150, and 700 ppm, respectively. However, liver-weight increases were not observed in females in any of the dose groups. Thus increases in liver weight occur after exposures that range from six to 24 months. Also, this effect was not fully reversible in males after the cessation of exposure. The NOAEL from this study is 10 ppm based on a 16 per cent increase in liver weight in males exposed to 30 ppm D4 for six months.

RCC (1995a, 1995b) also observed changes in other organs in studies with concentrations of 488 ppm and above. Also reported are adrenal weight increases of 12–30 per cent compared to controls, sometimes accompanied by an increased incidence of vaccuolation in the zona fasciculata. Also observed were thymus weight decreases of 14–30 per cent in comparison to controls, as have effects in the ovaries. A 28 day study resulted in corpora lutea counts were slightly reduced for one in ten control rats and, for treated rats, one in tem at 226 ppm, two in ten at 417 ppm, three in ten at 700 ppm, and four in six at 1154 and 1076 ppm. The significance of this finding is discussed in more detail in the context of the reproductive toxicity findings (Section 4.8.8). In two 90 day studies ovary weights reduced by 28 or 38 per cent compared to controls in rats that inhaled 700 or 898 ppm (Dow Corning, 1989; RCC, 1995b).

Overall, liver weight increase is the key systemic effect observed in inhalation studies in rats. An overall inhalation NOAEL for liver enlargement of 5 ppm (60 mg/m^3) is identified on the basis of a 14 per cent increase in liver weight at the next highest concentration of 10 ppm (121 mg/m^3) in a 90 day rat study.

4.4.5.2 Oral

Gavage studies of up to 14 days duration are available in rats and rabbits. The effects of long-term oral exposures have not been examined.

Sprague Dawley rats were treated by gavage with 25, 100, 400, or 1600 mg/kg/day D4 five days per week for 14 days (Dow Corning, 1990). Liver weights increased by more than

10 per cent in males at 400 and 1600 mg/kg/day. In females, liver weights increased by 8, 17, 24, and 24 per cent at 25, 100, 400, and 1600 mg/kg/day, respectively. A NOAEL of 25 mg/kg/day is identified on the basis that liver weights at this dose are within 10 per cent of control liver weights. At 1600 mg/kg/day terminal bodyweights in males and females reduced slightly to 83 and 89 per cent of control weights, respectively. Histopathology was not assessed in this study. In Sprague Dawley rats administered 1, 5, 20, or 100 mg/kg/day D4 in corn oil for four days a similar profile of enzymes was induced to that with phenobarbital (Zhang *et al*., 2000). A four-fold increase in CYP2B1/2 occurred in females at the lowest dose of 1 mg/kg/day D4. In this study relative liver weights in females given 20 and 100 mg/kg/day D4 increased by around 20 per cent in. Absolute weights are not reported. In terms of a NOAEL for liver weight increases, a dose of 25 mg/kg/day identified in the 14 day study is taken as the NOAEL for liver enlargement based on a 17 per cent increase in females at the next highest dose of 100 mg/kg/day (Dow Corning, 1990).

Liver weights were not affected in rabbits given up to 1000 mg/kg/day D4 for 14 days (Dow Corning, 1992; International Research and Development Corporation, 1993b). In this species the main finding is a reduction in food consumption and corresponding reduction in body weight. In dietary studies, palatability of the test substance can reduce food consumption. However, in the case of D4, reduced food consumption occurs in gavage studies and at high concentrations in inhalation studies, where palatability issues do not apply. The reduced food consumption may therefore represent a pharmacological effect because of the dopamine-like effects of D4.

Rabbits given 500 or 1000 mg/kg D4, seven days per week for 14 days consumed between 25 and 50 per cent of the amount of food consumed by controls, and terminal bodyweights were up to 20 per cent less than those of controls at both dose levels (Dow Corning, 1992). A NOAEL for reduced food consumption cannot be identified from this study. International Research and Development Corporation (1993b) studied a wider range of dose levels in a range-finding developmental toxicity study. In this study, food consumption was reduced to 73 and 57 per cent of control levels at 50 and 100 mg/kg/day D4, respectively, with no significant effect on overall bodyweight gain. At 500 and 1000 mg/kg/day severely reduced food consumption was thought to cause the increased incidence of spontaneous abortion and post-implantation loss. On the basis that the reduction in food consumption at 100 mg/kg/day has no impact on bodyweight gain, a NOAEL for reduced food consumption is identified at 100 mg/kg. In terms of the possible long-term consequences of this effect, when it occurs in inhalation studies, the effects are transient and reversible during a 90 day exposure period (RCC, 1995b).

Overall, liver weight increase is the key systemic effect observed in oral studies in rats. An overall oral NOAEL for liver enlargement of 25 mg/kg/day is identified on the basis of a 17 per cent increase in liver weight at the next highest dose of 100 mg/kg/day in a 14 day rat study.

4.4.5.3 Dermal

Bayer (1988) reported no adverse effects in one three week dermal exposure study in which male and female New Zealand white rabbits received doses of 0.1, 0.3, or 1 ml/kg undiluted D4 (equivalent to 96, 288, and 960 mg/kg), five days per week for three weeks (. The lack of any adverse effects in dermal exposure studies is consistent with the minimal dermal penetration measured for D4. The NOAEL for the effects of repeated dermal

exposure lies above 960 mg/kg/day, which is the highest dose administered in any study to date.

4.4.5.4 Summary of the effects of repeated exposure

Various studies give the effects of repeated exposure to D4 by all relevant routes. Inhalation of D4 produces local effects in the respiratory tract that indicate a mild irritant response at concentrations of 150 ppm or more. A NOAEL of 30 ppm (363 mg/m^3) was identified and can be used for the human health risk characterisation of local effects on the respiratory tract after repeated inhalation exposure to D4.

In relation to systemic effects, the key effect is liver enlargement and associated hypertrophy caused by phenobarbital-type enzyme induction. Liver enlargement occurs after both oral and inhalation exposures in rats. This effect is relevant to human health as liver-enzyme induction and liver enlargement do occur in humans who receive therapeutic doses of phenobarbital. As increases in liver weight greater than 10 per cent lie just outside the range of normal human variation, any such increases are considered to have adverse consequences for health. Very large increases in liver size can compress other abdominal organs, and enzyme induction can impair the normal response to other xenobiotics. Unlike the short-term reversible liver enlargement (≥10 per cent) caused by the related cyclosiloxane D5, increased liver weight caused by D4 was is maintained with exposures given for two years. A NOAEL of 5 ppm (60 mg/m^3), six hours per day and five days per week is identified for the inhalation route on the basis of a 14 per cent increase in relative liver weight at the next highest concentration of 10 ppm in a 90 day study in rats. A NOAEL of 25 mg/kg/day is identified for the oral route on the basis of a 17 per cent increase in liver weight at the next highest dose of 100 mg/kg/day in a 14 day study in rats.

No adverse effects are reported in rabbits treated via the dermal route with up to 960 mg/kg/day for three weeks, the highest dose tested to date.

4.4.6 Mutagenicity

Union Carbide (1993a, 1993b, 1994a, 1994b) report a variety of *in vitro* mutagenicity assays with D4, including a bacterial reverse-mutation assay in *Salmonella typhimurium*, DNA damage and repair assay in *E. coli,* a gene mutation assay in the yeast *Saccharomyces cerevisiae*, and a cytogenetics assay and sister chromatid exchange test, both in Chinese hamster ovary cells. All assays gave negative results. The mutagenic potential of D4 was also tested in a number of mouse lymphoma cell-line assays with and without metabolic activation. These tests include a gene mutation test, a sister chromatid exchange test, a chromosome aberration assay, and an alkaline elution assay. Ambiguous results were obtained in the chromosome aberration assay and the sister chromatid exchange test with metabolic activation only, and otherwise negative results were obtained.

A bone-marrow chromosome aberration assay in rats and mice gave negative results.

4.4.7 Carcinogenicity

There are no carcinogenicity data for D4 from humans. Battelle Toxicology Northwest (2004) assessed the carcinogenic potential of D4 in F344 rats in a single study. Groups of 60 rats per sex were exposed to 10, 30, 150, or 700 ppm, six hours per day, five days per week for up to two years. No neoplastic changes are reported in the respiratory tract or in the liver. These sites are identified as target tissues in repeated exposure studies. The only

neoplastic finding associated with exposure to D4 is uterine endometrial adenoma and adenocarcinoma. Uterine adenomas were found in 11 per cent (4 in 35) of females at 700 ppm. The adenomas were accompanied by an increased incidence of endometrial epithelial hyperplasia that affected 80 per cent (28 in 35) rats compared to 19 per cent (11 in 58) in controls. One endometrial adenocarcinoma also arose in a female rat exposed to 150 ppm for 12 months with a recovery period of 12 months, as did one endometrial adenoma in a female rat exposed to 30 ppm for 12 months and allowed the same recovery period. Endometrial epithelial hyperplasia also occurred in this group, but there was no clear dose relationship. No uterine adenomas were reported in animals culled after 12 months of exposure or in concurrent control groups. It seems inconsistent that treatment-related tumours can occur at 30 ppm and 150 ppm in animals exposed for 12 months and allowed a 12 month recovery period, and yet no tumours occurred in animals exposed to this regime at 700 ppm and none in those exposed to 30 ppm or 150 ppm for 24 months. Equally, it is difficult to dismiss the tumours since they are of the same type as the treatment-related ones that occurred at 700 ppm. On this basis it is assumed that these tumours are treatment related.

Mechanistic studies indicate that the endometrial tumours arise because D4 acts as a dopamine agonist (CES, 2005c). By maintaining dopaminergic inhibition of prolactin secretion, female reproductive senescence is delayed, which leads to prolonged stimulation of the endometrium and eventually to tumours. Differences in the reproductive ageing process between humans and rodents render this mechanism irrelevant to humans (CES, 2005c). It is not clear whether tumours that occur after D4 exposure are relevant to other species exposed via the food chain. However, because the carcinogenic effect occurs late in life, it is not an effect that influences the sustainability of a population. It is therefore not necessary to take the carcinogenicity of D4 into account in a risk assessment for secondary poisoning of wildlife exposed via the food chain.

4.4.8 Toxicity for reproduction

There are no data for humans on the reproductive effects of D4. However, a series of studies was conducted to examine reproductive and developmental endpoints in rats and developmental toxicity in rabbits.

4.4.8.1 Fertility

The effects of D4 on fertility were examined in two range-finding studies, male and/or female cross-over studies, and 'phased female' studies, as well as in a two-generation study (Holson *et al.*, 1995, 1996, 1997a, 1997b; Stump *et al.*, 1997, 1998, 1999, 2001). In these studies, male and/or female Sprague Dawley rats were exposed by whole-body vapour inhalation to D4 at concentrations that ranged from 70 to 700 ppm for six hours per day, seven days per week. The general protocol for each study was similar and included exposure for at least 28 or 70 days prior to mating, and exposure to females continued in some studies throughout gestation and lactation.

In fertility studies, the major findings in females exposed to 500 ppm or more were statistically significant treatment-related decreases in the number of corpora lutea, number of uterine implantation sites, total number of pups born, and mean live litter size (Holson *et al.*, 1995, 1996, 1997a; Stump *et al.*, 1998, 2001). These effects are likely to be interrelated. The mean live litter size in the 700 ppm exposure group was consistently 60–70 per cent of the control values. At 500 ppm, litter size was around 80–90 per cent of control values and at 300 ppm in the two-generation study the litter size was 89.5 per cent of control in the F_1

generation and 92 per cent of control in the F_2 generation (Stump *et al.*, 2001). Although the mean live litter size was reduced, the number of live births as a percentage of the total number of pups born compares with control values in each case.

No effects on the number of uterine implantation sites, the litter size, or the mean live litter size occurred in male cross-over studies in which males were mated to unexposed females (Holson *et al.*, 1997b; Stump *et al.*, 1997). Exposure to D4 did not affect sperm production, motility, or morphology, nor did it result in either weight or histopathological changes of male reproductive or accessory sex organs. It is therefore concluded that the effects on litter size are not male mediated.

In addition to the studies described above in which animals were exposed to D4 throughout pre-mating, mating, gestation, and lactation, studies in which female rats were exposed during selected phases of the reproductive cycle (Stump *et al.*, 1998, 1999) were conducted. These were designed to identify the critical portions of the reproductive cycle in female Sprague Dawley rats during which exposure to D4 must occur for the litter size to be affected.

The first of these studies involved exposure of separate groups beginning (Stump *et al.*, 1998):

- at least 28 days prior to mating and continuing through to gestation day 19 (overall phase);
- 31 days prior to mating and stopping three days prior to mating (ovarian phase);
- three days prior to mating and continuing to gestation day three (fertilisation phase) or between gestation days two and five (implantation phase).

In both the overall phase and the fertilisation phase the numbers of corpora lutea, uterine implantation sites, and foetuses were reduced, along with an increase in pre- and post-implantation loss. There was no effect on fertility parameters in females exposed during the ovarian or implantation phases, which suggest that the key events occur during the three days before and after mating.

This critical period was confirmed in the subsequent study in which groups of females were exposed to 700 ppm D4 six hours per day for single days or groups of days that covered a period from four days before mating to gestation day three (Stump *et al.*, 1999). Only in the group exposed for six days before and three days after mating were the numbers of corpora lutea and implantation sites reduced. Also, the number of small implantation sites in this group substantially increased. Numbers of corpora lutea were not affected in rats exposed once on days four, three, two, or one before mating. However, there was a treatment-related reduction in pregnancy rate in females exposed on day one prior to mating. The ovaries from this group had a normal complement of corpora lutea, but only 65 per cent of females with evidence for mating became gravid compared to 90 per cent or more in all other groups.

That no effect in females exposed to D4 prior to, but not during, the critical window surrounding mating is observed indicates that it is reversible. In September 2006 specialised experts discussed the mechanism and relevance for human health of these findings in the context of classification and labelling. These experts were of the opinion that the mechanism behind the reproductive effects of D4 could be relevant to human health. On the basis that the reduction in live litter size at 300 ppm is around 10 per cent or less compared to controls, this is taken as the NOAEL for this effect.

The effects of D4 via h oral or dermal routes on fertility have not been studied.

4.4.8.2 Development

Developmental toxicity studies by the inhalation and oral routes have been conducted. In whole-body inhalation studies, rats were exposed to D4 at concentrations in the range 10–700 ppm six hours per day on gestation days 6–15 and rabbits were exposed to D4 at concentrations in the same range (the top concentration used in the main study was 500 ppm) six hours per day on gestation days 6–18 (International Research and Development Corporation, 1993a, 1993c, 1993d). In an oral range-finding study, rabbits were administered gavage doses of 50–1000 mg/kg/day on gestation days 7–19 (International Research and Development Corporation, 1993b). In each study there was evidence for maternal toxicity at the upper end of the dose range, but no evidence for any adverse developmental effects caused by D4.

4.4.8.3 Summary

There is no evidence that D4 has any specific developmental effects. The key reproductive effect of D4 is on fertility. In rats, D4 reduces numbers of corpora lutea, which results in a reduction in live litter sizes. The critical of exposure for this effect to occur is in the three days prior to mating. There is no effect in rats exposed prior to but not during this critical period, which indicates that the effect is reversible. A NOAEL of 300 ppm is identified on the basis of a two-generation study that showed a reduction in live litter size of 10 per cent or less at this concentration and a reduction of 10–20 per cent at the next concentration, 500 ppm.

4.4.9 Summary of mammalian toxicity

Studies in the rat show that around 5 per cent of inhaled D4 is absorbed; in humans 6–17 per cent may be absorbed. In rats around 50 per cent of an oral dose given in corn oil is absorbed. In rats and humans only around 1 per cent of the applied dose of D4 is absorbed across the skin, with absorption being limited by evaporation from the skin. Absorbed D4 is distributed widely throughout the body, with some preferential storage in fat. The potential for bioaccumulation through enzyme induction is limited. D4 is metabolised – in rats the two major metabolites are dimethylsilanediol and methylsilanetriol, both of which were also identified in humans. The main routes of elimination for D4 and its metabolites are in the urine and exhaled air, and faeces are a minor route.

D4 is of low acute toxicity. The LC_{50} for a single four hour inhalation exposure in the rat is 36 mg/l. The oral LD_{50} value in the rat is above 4800 mg/kg and the dermal LD_{50} value in the rat is above 2400 mg/kg.

D4 is not a skin irritant in humans and is not a skin or eye irritant in animals. There is no evidence from human volunteers that inhaled D4 causes sensory respiratory tract irritation.

D4 is not a skin sensitiser and, given what is generally known about cyclosiloxanes, D4 is be predicted to show asthmagenic potential.

The effects of repeated exposure to D4 have been studied by all relevant routes. Inhalation of D4 causes respiratory tract irritation in rats. A NOAEL of 30 ppm (363 mg/m^3) for local effects on the respiratory tract is identified on the basis of a two year inhalation study. At the next highest exposure level of 150 ppm, an increased incidence of eosinophilic globules in the nasal epithelium indicates a mild rhinitis response. The NOAEL of 30 ppm is used in the human health risk assessment for the respiratory effects of repeated inhalation of D4.

In relation to systemic effects, the key effect is liver enlargement and associated hypertrophy caused by phenobarbital-type enzyme induction. Liver enlargement occurs after both oral and inhalation exposures in rats. This effect is relevant to human health as liver enzyme induction and liver enlargement occur in humans who receive therapeutic doses of phenobarbital. As increases in liver weight greater than 10 per cent lie just outside the range of normal human variation, any such increases are considered adverse to health. Furthermore, very large increases in liver size can compress other abdominal organs, and enzyme induction can alter the normal response to other xenobiotics. An inhalation NOAEL of 5 ppm (60 mg/m^{-3}) is identified on the basis of a 90 day study that shows a 14 per cent increase in liver weights at 10 ppm (121 mg/m^{-3}). An oral NOAEL of 25 mg/kg/day is be identified on the basis of a 17 per cent increase in liver weight at 100 mg/kg/day in a 14 day gavage study in rats.

No adverse effects are reported in rabbits given dermal doses of up to 960 mg/kg/day for three weeks – this is the highest dose tested.

D4 does not have mutagenic potential either *in vitro* or *in vivo*.

D4 causes uterine tumours in F344 rats, but the underlying mechanism is not relevant to humans. Since the carcinogenic effect occurs late in life, it is not an effect that influences the sustainability of a population. It is therefore not necessary to take the carcinogenicity of D4 into account in a risk assessment for secondary poisoning of wildlife exposed via the food chain.

There is no evidence that D4 has any specific developmental effects. The key reproductive effect of D4 is on fertility. In rats, D4 reduces numbers of corpora lutea, which results in a reduction in live litter sizes. The critical exposure period for this effect to occur is in the three days prior to mating. The mechanism behind the reproductive effects of D4 could be relevant to human health. A NOAEL of 300 ppm (equivalent to an extrapolated oral NOAEL of 105 mg/kg/day) is identified on the basis of a two-generation study that showed a reduction in live litter size of 10 per cent or less at this concentration and a reduction of 10–20 per cent at the next concentration, 500 ppm. This NOAEL is, however, higher than that set for liver enlargement, and therefore any possible adverse effect on fertility should be protected against.

Overall, the critical effects of exposure to D4 are chronic respiratory tract irritation after inhalation exposure, liver weight increases after repeated exposure, and a potential concern for fertility. In relation to the local effects on the respiratory tract, a NOAEL of 30 ppm is identified on the basis of a two year rat study. In relation to the systemic effects on the liver after repeated exposure a NOAEL of 25 mg/kg/day is identified from a 14 day oral study with rats. For the potential effects on fertility a NOAEL of 105 mg/kg/day is selected on the basis of a two-generation study in rats.

4.4.10 Derivation of PNECoral

The lowest NOAEL for D4 relevant to secondary poisoning is 25 mg/kg body weight/day for effects on the liver after repeated oral exposure. Using the conversion factors given in the TGD (20 for rats older than six weeks), a daily dose of 25 mg/kg body weight/day is equivalent to a daily concentration of 500 mg/kg food.

As the NOAEL was determined in a study of relatively short duration (14 days exposure) a relatively high AF is needed as it is possible that the NOAEL could be lower after exposure for a longer term. The TGD recommends an AF of 300 be used for a NOAEL based on a 28 day study, and this value is assumed here for the result from the 14 day study (no AF is listed in the TGD for a 14 day study). This approach is consistent with that used to define a

margin of safety in the characterisation for human health risk (see Section 5.6). Therefore a PNEC of 1.7 mg/kg food is estimated for D4.

4.5 Classification for environmental hazard

D4The currently agreed classification of D4 for environmental and health hazard is:

- environment:
  - Dangerous for the environment
  - R53: May cause long-term adverse effects in the aquatic environment;
- human health
  - Repro. Cat 3
  - R62: Possible risk of impaired fertility.

5 Risk characterisation

5.1 Aquatic compartment

5.1.1 Risk characterisation ratios for surface water

The PNEC for water is 0.44 µg/l. The risk characterisation ratios that result are summarised in Table 5.1.

Table 5.1 Risk characterisation ratios for surface water

Scenario	PEC (µg/l)	Risk characterisation ratio
Production and on-site use as an intermediate – UK site	3.9	8.9
Off-site use as an intermediate – polymers – wet process – UK sites	7.5×10^{-3}	0.017
Off-site use as an intermediate – polymers – wet process – EU sites	2.4×10^{-3}	5.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	2.4×10^{-3}	5.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – EU sites	2.4×10^{-3}	5.5×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	2.4×10^{-3}	5.5×10^{-3}
Personal care products – formulation – UK sites	2.5×10^{-3}	5.7×10^{-3}
	2.7×10^{-3}	6.1×10^{-3}
	2.5×10^{-3}	5.7×10^{-3}
	2.5×10^{-3}	5.7×10^{-3}
	2.8×10^{-3}	6.4×10^{-3}
	3.1×10^{-3}	7.0×10^{-3}
	3.9×10^{-3}	8.8×10^{-3}
	2.9×10^{-3}	6.6×10^{-3}
	2.8×10^{-3}	6.4×10^{-3}
	2.8×10^{-3}	6.4×10^{-3}
	2.8×10^{-3}	6.4×10^{-3}
	2.7×10^{-3}	6.1×10^{-3}
Personal care products – formulation – generic site (non-UK)	0.018	0.041
Personal care products – use by general public	9.0×10^{-3}	0.020
Household products – formulation	7.6×10^{-3}	0.017
Household products – use	3.0×10^{-3}	6.8×10^{-3}
Regional	2.4×10^{-3}	5.5×10^{-3}

Notes: Risk characterisation ratios >1 are obtained for production and on-site use as an intermediate only. No risk is indicated from the other scenarios considered.

5.1.2 Risk characterisation ratios for wastewater treatment plant micro-organisms

The PNEC for WWTPs is >100 mg/l. The risk characterisation ratios that result are summarised in Table 5.2.

Table 5.2 Risk characterisation ratios for wastewater treatment plants

Scenario	PEC (mg/l)	Risk characterisation ratio
Production and on-site use as an intermediate – UK site	0.010	$<1 \times 10^{-4}$
Off-site use as an intermediate – polymers – wet process – UK sites	3.6×10^{-4}	$<3.6 \times 10^{-6}$
Off-site use as an intermediate – polymers – wet process – EU sites	1.2×10^{-9}	$<1.2 \times 10^{-9}$
Off-site use as an intermediate – polymers – dry process – UK sites	0	<<1
Off-site use as an intermediate – polymers – dry process – EU sites	0	<<1
Off-site use as an intermediate – silica – UK and EU sites	0	<<1
Personal care products – formulation – UK sites	1.1×10^{-6}	<1.1 v 10^{-8}
	3.4×10^{-6}	$<3.4 \times 10^{-8}$
	7.7×10^{-7}	$<7.7 \times 10^{-9}$
	1.0×10^{-6}	$<1.0 \times 10^{-8}$
	4.3×10^{-6}	$<4.3 \times 10^{-8}$
	7.5×10^{-6}	$<7.5 \times 10^{-8}$
	1.6×10^{-5}	$<1.6 \times 10^{-7}$
	5.0×10^{-6}	$<5.0 \times 10^{-8}$
	4.1×10^{-6}	$<4.1 \times 10^{-8}$
	4.2×10^{-6}	$<4.2 \times 10^{-8}$
	4.7×10^{-6}	$<4.7 \times 10^{-8}$
	3.8×10^{-6}	$<3.8 \times 10^{-8}$
Personal care products – formulation – generic site (non-UK)	1.6×10^{-4}	$<1.6 \times 10^{-6}$
Personal care products – use by general public	6.8×10^{-5}	$<6.8 \times 10^{-7}$
Household products – formulation	5.4×10^{-5}	$<5.4 \times 10^{-7}$
Household products – use	6.1×10^{-6}	$<6.1 \times 10^{-8}$

Based on this worst-case analysis the risk to WWTPs is low.

5.1.3 Risk characterisation ratios for sediment

The PNEC for sediment is 0.12 mg/kg wet weight. The risk characterisation ratios that result are summarised in Table 5.3.

Risk characterisation ratios >1 are obtained for production and on-site use as an intermediate only. No risk is indicated from the other scenarios considered.

Table 5.3 Risk characterisation ratios for sediment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratios
Production and on-site use as an intermediate – UK site	1.5 [1]	13
Off-site use as an intermediate – polymers – wet process – UK sites	2.8×10^{-3}	0.024
Off-site use as an intermediate – polymers – wet process – EU sites	8.8×10^{-4}	7.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	8.8×10^{-4}	7.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – EU sites	8.8×10^{-4}	7.5×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	8.8×10^{-4}	7.5×10^{-3}
Personal care products – formulation – UK sites	9.2×10^{-4}	7.9×10^{-3}
	1.0×10^{-3}	8.5×10^{-3}
	9.1×10^{-4}	7.8×10^{-3}
	9.2×10^{-4}	7.9×10^{-3}
	1.0×10^{-3}	8.5×10^{-3}
	1.2×10^{-3}	0.010
	1.5×10^{-3}	0.013
	1.1×10^{-3}	9.4×10^{-3}
	1.0×10^{-3}	8.5×10^{-3}
	1.0×10^{-3}	8.5×10^{-3}
	1.1×10^{-3}	9.4×10^{-3}
	1.0×10^{-3}	8.5×10^{-3}
Personal care products – formulation – generic site (non-UK)	6.7×10^{-3}	0.057
Personal care products – use by general public	3.3×10^{-3}	0.028
Household products – formulation	2.8×10^{-3}	0.024
Household products – use	1.1×10^{-3}	9.4×10^{-3}
Regional	1.7×10^{-3}	0.015

Note [1]Further monitoring data for sediment at the UK production site became available very recently (Environment Agency, personal communication, 2005). The results are from the EA 04/05 monitoring programme to be published in due course. The levels of D4 found in two samples (collected in February 2005) were 0.33 and 0.39 mg/kg wet weight (1.7–2.0 mg/kg dry weight). These levels also lead to a risk characterisation ratio >1.

5.1.4 Uncertainties and possible refinements

On the basis of the available data, the risk characterisation ratios for surface water and sediment for production and on-site use as an intermediate for polymers are >1. The assessment for production and on-site use as an intermediate is based on site-specific

monitoring data for a site in the UK. Relatively few monitoring data are available and so there is some uncertainty in the estimates obtained using the approach taken. This indicates a need to refine the PEC calculations for these scenarios. If refinement of the PEC is insufficient to resolve the concern for the sediment compartment, then further toxicity testing with sediment organisms is needed to refine the PNEC for this endpoint.

It is not possible to further refine the PNEC for surface water.

5.1.5 Conclusions for the aquatic compartment

The risks to WWTPs are thought to be low based on the information currently available and a default exposure estimate. For surface water and sediment, risk characterisation ratios >1 are used for production and on-site use as an intermediate. The risks to surface water and sediment from the other scenarios considered are low.

Further information is needed to refine the exposure assessment. This information includes (but is not limited to) further monitoring data of emissions from the UK production site.

In addition, if the PECs for sediment cannot be refined sufficiently, further long-term sediment toxicity testing should be considered. As D4 has a high log K_{ow}, any future sediment toxicity testing should include the recommendation in the TGD that no supplemental feeding be used. However, for the scenario for production and on-site use as an intermediate, revision of the PNEC for sediment alone is unlikely to result in a risk characterisation ratio <1 without further information to refine the PEC for sediment.

5.2 Terrestrial compartment

5.2.1 Risk characterisation ratios

A PNEC of 0.16 mg/kg wet weight is derived for D4 using the equilibrium partitioning approach. The log K_{ow} of D4 is >5 and the TGD recommends that for such chemicals, to account for the possibility of direct ingestion of soil-bound substance, the risk characterisation ratios that result be increased by a factor of ten when using the equilibrium partitioning approach. The risk characterisation ratios that result (increased by a factor of ten) are summarised in Table 5.4.

Based on this worst-case assessment, no risk characterisation ratio >1 is obtained. Therefore it is concluded that all scenarios lead to a low risk.

Table 5.4 Risk characterisation ratios for the terrestrial compartment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratio
Production and on-site use as an intermediate – UK site	7.3×10^{-5}	4.6×10^{-3}
Off-site use as an intermediate – polymers – wet process – UK sites	3.0×10^{-4}	0.019
Off-site use as an intermediate – polymers – wet process – EU sites	1.4×10^{-6}	8.9×10^{-5}
Off-site use as an intermediate – polymers – dry process – UK sites	2.5×10^{-7}	1.6×10^{-5}
Off-site use as an intermediate – polymers – dry process – EU sites	2.7×10^{-5}	1.7×10^{-5}
Off-site use as an intermediate – silica – UK and EU sites	8.1×10^{-7}	5.1×10^{-5}
Personal care products – formulation – UK sites	1.0×10^{-6}	6.6×10^{-5}
	2.9×10^{-6}	1.9×10^{-4}
	7.4×10^{-7}	4.7×10^{-5}
	9.5×10^{-7}	6.0×10^{-5}
	3.7×10^{-6}	2.3×10^{-4}
	6.4×10^{-6}	4.0×10^{-4}
	1.4×10^{-5}	8.6×10^{-4}
	4.3×10^{-6}	2.7×10^{-4}
	3.5×10^{-6}	2.2×10^{-4}
	3.6×10^{-6}	2.3×10^{-4}
	4.0×10^{-6}	2.5×10^{-4}
	3.2×10^{-6}	2.0×10^{-4}
Personal care products – formulation – generic site (non-UK)	1.4×10^{-4}	8.5×10^{-3}
Personal care products – use by general public	5.7×10^{-5}	3.6×10^{-3}
Household products – formulation	4.5×10^{-5}	2.8×10^{-3}
Household products – use	5.6×10^{-6}	3.3×10^{-4}
Regional – agricultural soil	8.4×10^{-4}	0.053
Regional – natural soil	9.7×10^{-8}	6.0×10^{-6}
Regional – industrial soil	9.7×10^{-8}	6.0×10^{-6}

5.2.2 5.2.2 Uncertainties and possible refinements

There are considerable uncertainties over both the PECs and the PNEC used in the assessment, as the approach taken effectively represents a worst-case one. A number of possible refinements could be undertaken, as outlined below. However, as no risks are identified using the worst-case approach, further work to address these uncertainties and refinements is a low priority at this time.

As discussed in Section 0, the actual degradation rate in soil for this substance is uncertain. The PECs used in the risk characterisation are all estimated assuming no degradation in soil. However, under dry soil conditions significant degradation of D4 is expected. The

analysis carried out in Section 0 indicates that under these conditions the predicted local concentrations (and hence subsequent PEC/PNEC ratios) may be lower by around a factor of two. Thus the effect of this uncertainty on the conclusions that can be drawn for the local assessment is minimal. The uncertainty in the degradation rate in soil also impacts on the predicted regional concentrations and, as no risk is predicted even assuming no degradation, similar conclusions are drawn for this endpoint if the substance degrades more rapidly than assumed.

A further consideration related to the spreading of sewage sludge is that, although a significant fraction of D4 is predicted to be adsorbed to sewage sludge during wastewater treatment, some of this could be lost (e.g. by volatilisation or hydrolysis) during subsequent treatment and handling of the sludge prior to application to land. For example, stabilisation of the sludge with lime raise the pH to around 12, conditions under which rapid hydrolysis of D4 may occur, or pasteurisation (by heating to 55–70°C for 30 minutes to four hours) may be carried out. Several other treatments are also commonly used (e.g. mesophilic anaerobic digestion, thermophilic aerobic digestion, composting, dewatering, and storage) whereby the sludge is treated and/or stored for several days [typically 7-–4 days, but up to three months for liquid storage, sometimes at elevated temperatures (35–55°C)] prior to spreading on land. Therefore the instantaneous concentration in sewage sludge predicted during wastewater treatment may not reflect the actual concentration in sewage sludge applied to land. Actual measurements in sewage sludge may be useful in this respect.

The risk characterisation ratios are currently increased by a factor of ten to account for the possible direct ingestion of soil-bound substance (as recommended in the TGD). This is based on the high log K_{ow} of D4 (log K_{ow} 5.1).

It is also possible to refine the PNEC for soil by carrying out long-term toxicity testing with soil organisms. However, as no risks are currently identified, there is no need for further revision of the PNEC in this case (also, soil toxicity testing of D4 is very difficult because of its high volatility).

It is possible that D4 could be formed in soil by the degradation of PDMS fluids and other siloxane polymers. A preliminary assessment of this potential source (see Section 0) indicates that the amounts of D4 that could be volatilised from soil via this process are likely to be small compared with other sources of D4. However, the uncertainties and simplifications in the approach taken are considerable, and little or no information is available on the breakdown of PDMS fluids and other siloxane polymers in landfills (landfills appear to be a major route of disposal for some of these polymers). It is currently assumed that such products are relatively stable under landfill conditions. In addition, it is not currently possible to estimate the amount of D4 that could be in the soil itself as a result of these processes. A further, in-depth, assessment of the use pattern, emission sources, and fate of PDMS and other siloxane polymers is needed to provide a more refined estimate of the potential emissions of D4 from this source. This is beyond the scope of the current risk assessment.

5.2.3 Conclusions for soil

Based on this worst-case assessment, no risks to the soil compartment are identified from the production and use of D4. Some uncertainties are associated with this assessment, but the risk characterisation here indicates that further work to address these uncertainties is not necessary at this time.

5.3 Atmospheric compartment

5.3.1 Conclusions for the atmosphere

No PNEC can be derived for the atmospheric compartment. The predicted concentrations in the atmosphere are generally low and so direct toxic effects are not expected.

Although D4 is reactive in the atmosphere, the half-life for the reaction is sufficiently long (estimated as around 14 days) that transport to remote regions could occur. This coupled with the high BCF (12,400 l/kg) for fish and the lack of biodegradability mean that D4 could possibly meet at least some of the screening criteria in relation to persistent organic pollutants (POPs). For example, the Stockholm Convention (UNEP, 2004) contains the screening criteria (among others):

- Persistence: evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months.
- Bioaccumulation: evidence that the BCF or bio-accumulation factor in aquatic species for the chemical is greater than 5000 or, in the absence of such data, that the log Kow is greater than five.
- Potential for long-range environmental transport: environmental fate properties and/or model results that demonstrate the chemical has a potential for long-range environmental transport through air, water, or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days.
- Adverse effects: toxicity or ecotoxicity data that indicate the potential for damage to human health or the environment.

The available information for D4 indicates that it could meet these screening criteria for bioaccumulation (fish BCF = 12,400 l/kg) and adverse effects. In relation to the persistence criteria, the most relevant data are probably the half-life for hydrolysis in surface water (e.g. 16.7 days at pH 7 and 12°C) and the half-life in sediment (thought to approach 120 days based on the results of a preliminary study). These half-lives are considerably shorter than the screening criteria above.

For long-range environmental transport, although D4 has the potential to be transported long distances via the atmosphere (i.e. the substance has a high Henry's law constant and an atmospheric half-life of around 14 days), the high Henry's law constant also means that it has a low potential for redeposition to surface media in remote regions. For example, Di Toro and Hellweger (1999) investigated the role of Henry's law constant in long-range transport and subsequent deposition in remote areas. D4 was used as an example substance in the report. Di Toro and Hellweger (1999) conclude that substances with high Henry's law constants (>1 on a dimensionless basis) are unlikely to be deposited in remote regions, even if they have very long degradation half-lives (up to three years) because most of the mass (around 99 per cent) remains in the atmosphere. The dimensionless Henry's law constant for D4 is around 490 at 25°C. Similar behaviour of D4 can be inferred from the modelling work of Klasmeier *et al.* (2004, 2006), Fenner *et al.* (2005), and Wania (2006), and the recent modelling studies on D4 by Xu *et al*. (2007b, 2007c) using the GLOBOPOP and OECDPov and LRTP screening tool (see Section 5.5.2). Similar conclusions are also

drawn for D5 based on the results of several different global models (Environment Agency, 2008a).

In relation to long-range atmospheric transport also relevant is the possibility of adsorption to atmospheric particulates with subsequent wet and dry deposition of particle-bound D4. The available (modelled) information reported in Section 3.2.1 indicates that, in air, D4 is expected to be mainly in the vapour phase, with only a small fraction associated with the water and particulate phases. In addition, experimental data available for D5, which has a lower Henry's law constant and a higher log K_{ow} than D4 (Environment Agency, 2008a), indicate that this substance is associated mainly with the gaseous phase, even at low temperatures (down to 0°C). On this basis it is expected that the vast majority of D4 in the atmosphere is in the gaseous phase, and so wet and dry deposition of particle-bound D4 is likely to be only a minor process.

In addition to this, the bioaccumulation potential for D4 in predators (e.g. mammals and birds) through breathing air appears to be much lower than may be expected on the basis of the high fish BCF (and log K_{ow}) alone, particularly in relation to inhalation exposure (see Section 3.2.9).

In conclusion, it is unlikely that D4 meets the POPs criteria and therefore the risk from long-range atmospheric transport should be low.

5.4 Non-compartment specific effects relevant to the food chain (secondary poisoning)

5.4.1 Risk characterisation ratios

The PNEC for secondary poisoning is estimated as 1.7 mg/kg food. As discussed earlier, the interpretation of the available toxicity data for D4 is not straightforward. In particular, the data used to derive the PNEC are based on liver weight increase without any evidence of an accompanying liver damage and the approach used assumes that an increase in liver weight alone may impair survival in the wild if the increase is sufficiently large. The risk characterisation ratios that result are summarised in Table 5.5.

Based on the worst-case risk characterisation ratios, the risk of secondary poisoning from the earthworm food chain appears to be low.

The worst-case risk characterisation ratios are >1 for the fish food chain for production and on-site use as an intermediate only.

5.4.2 Uncertainties and possible refinements

It is not straightforward to interpret the effects seen in the available oral exposure mammalian toxicity studies. The PNEC is derived on the basis of liver enlargement in rats caused by oral exposure seen. This liver weight increase occurs without evidence of any accompanying liver damage and the approach used here assumes that an increase in liver weight alone may impair survival in the wild if the increase is sufficiently large.

There is a large uncertainty over the BMF used for the fish food chain. The default value is 10, which was shown to not be appropriate for D4. The BMF for D4 of 4.6 used in the assessment is both growth corrected and lipid normalised. Lower BMFs for D4 are obtained without these corrections.

The analysis carried out in Appendix A indicates that the assessment for secondary poisoning is relatively insensitive to the log K_{ow} value used.

Table 5.5 Risk characterisation ratios for secondary poisoning

Scenario	Fish[1]		Earthworms	
	PEC (mg/kg)	Risk characterisation ratio	PEC (mg/kg)	Risk characterisation ratio
Production and on-site use as an intermediate – UK site	112	67	0.048	0.029
Off-site use as an intermediate – polymers – wet process – UK sites	0.21	0.13	0.046	0.028
Off-site use as an intermediate – polymers – wet process – EU sites	0.17	0.10	0.044	0.026
Off-site use as an intermediate – polymers – dry process – UK sites	0.17	0.10	0.044	0.026
Off-site use as an intermediate – polymers – dry process – EU sites	0.17	0.10	0.045	0.027
Off-site use as an intermediate – silica treatment – UK and EU sites	0.17	0.10	0.044	0.026
Personal care products – formulation – UK sites	0.17	0.10	0.044	0.026
	0.17	0.10	0.044	0.026
	0.17	0.10	0.044	0.026
	0.17	0.10	0.044	0.026
	0.18	0.11	0.044	0.026
	0.19	0.11	0.044	0.026
	0.21	0.13	0.044	0.026
	0.18	0.11	0.044	0.026
	0.18	0.11	0.044	0.026
	0.18	0.11	0.044	0.026
	0.18	0.11	0.044	0.026
	0.18	0.11	0.044	0.026
Personal care products – formulation – generic site (non-UK)	0.61	0.37	0.045	0.027
Personal care products – use by general public	0.39	0.23	0.045	0.027
Household products – formulation	0.31	0.19	0.045	0.027
Household products – use	0.19	0.11	0.044	0.026

Note: [1]The calculations for fish include a BMF of 4.6.

5.4.3 Conclusions for predators

Based on this worst-case exposure assessment the risk from secondary poisoning appears to be low for the terrestrial food chain.

For the aquatic food chain the risk characterisation ratio is >1 for the fish food chain for production and on-site use as an intermediate only.

5.5 Marine compartment

5.5.1 Risk characterisation ratios

PNECs used for the marine compartment are 0.044 µg/l for marine water, 0.012 mg/kg wet weight for sediment, and 1.7 mg/kg food for secondary poisoning. The risk characterisation ratios that result are summarised in Table 5.6.

Based on this worst-case analysis, two local scenarios (production and on-site use as an intermediate and the generic scenario for formulation of personal care products) lead to risk characterisation ratios >1 for marine water and sediment. In addition, the local scenario for production and on-site use as an intermediate also leads to risk characterisation ratios >1 for secondary poisoning in predators and top predators. For formulation of personal care products, site-specific information, available for all sites in the UK that carry out this application, indicates a low risk to marine water and sediment. Thus the reliability of the generic scenario for formulation of personal care products at sites in other parts of the EU is suspect. Indeed, information provided on sites in the EU that formulate personal care products that contain D5 generally show a similar range of PEC values as that for the UK sites (Environment Agency, 2008a). Therefore the risks to the marine environment of D4 from formulation sites in other parts of the EU are low, as for the UK sites.

Table 5.6 Risk characterisation ratios for the marine environment

Scenario	Water		Sediment		Predators[1]		Top predators[2]	
	PEC (µg/l)	RCR	PEC (mg/kg wet weight)	RCR	PEC (mg/kg)	RCR	PEC (mg/kg)	RCR
Production and on-site use as an intermediate - UK site	0.099	2.3	0.037	3.2	2.8	1.7	3.2	1.9
Off-site use as an intermediate – polymers – wet process – UK sites	3.6×10^{-3}	0.082	1.3×10^{-3}	0.11	0.044	0.026	0.10	0.060
Off-site use as an intermediate – polymers – wet process – EU sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}	0.011	6.6×10^{-3}	0.063	0.038
Off-site use as an intermediate – polymers – dry process – UK sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}	0.011	6.6×10^{-3}	0.063	0.038
Off-site use as an intermediate – polymers – dry process – EU sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}	0.011	6.6×10^{-3}	0.063	0.038
Off-site use as an intermediate – silica – UK and EU sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}	0.011	6.6×10^{-3}	0.063	0.038
Personal care products – formulation – UK sites	1.7×10^{-4}	3.9×10^{-3}	6.4×10^{-5}	5.5×10^{-3}	0.012	7.2×10^{-3}	0.063	0.038
	1.9×10^{-4}	4.5×10^{-3}	7.2×10^{-5}	6.2×10^{-3}	0.012	7.2×10^{-3}	0.064	0.038
	1.7×10^{-4}	3.9×10^{-3}	6.3×10^{-5}	5.4×10^{-3}	0.011	6.6×10^{-3}	0.063	0.038
	1.7×10^{-4}	3.9×10^{-3}	6.3×10^{-5}	5.4×10^{-3}	0.012	7.2×10^{-3}	0.063	0.038
	2.0×10^{-4}	4.5×10^{-3}	7.5×10^{-5}	6.4×10^{-3}	0.012	7.2×10^{-3}	0.064	0.038
	2.3×10^{-4}	5.5×10^{-3}	8.7×10^{-5}	7.4×10^{-3}	0.013	7.8×10^{-3}	0.065	0.039
	3.2×10^{-4}	7.3×10^{-3}	1.2×10^{-4}	0.010	0.016	9.6×10^{-3}	0.068	0.041
	2.1×10^{-4}	4.8×10^{-3}	7.8×10^{-5}	6.7×10^{-3}	0.013	7.8×10^{-3}	0.064	0.038
	2.0×10^{-4}	4.5×10^{-3}	7.5×10^{-5}	6.4×10^{-3}	0.012	7.2×10^{-3}	0.064	0.038

Scenario	Water		Sediment		Predators[1]		Top predators[2]	
	PEC (µg/l)	RCR	PEC (mg/kg wet weight)	RCR	PEC (mg/kg)	RCR	PEC (mg/kg)	RCR
	2.0×10^{-4}	4.5×10^{-3}	7.5×10^{-5}	6.5×10^{-3}	0.012	7.2×10^{-3}	0.064	0.038
	2.1×10^{-4}	4.8×10^{-3}	7.7×10^{-5}	6.6×10^{-3}	0.013	7.8×10^{-3}	0.064	0.038
	2.0×10^{-4}	4.5×10^{-3}	7.3×10^{-5}	6.2×10^{-3}	0.012	7.2×10^{-3}	0.064	0.038
Personal care products – formulation – generic site (non-UK)	0.044	1.0	0.016	1.4	1.3	0.78	1.5	0.90
Personal care products – use by general public	8.2×10^{-4}	0.019	3.0×10^{-4}	0.026	0.034	0.020	0.088	0.053
Household products – formulation	0.015	0.34	5.5×10^{-3}	0.47	0.43	0.26	0.53	0.32
Household products – use	2.2×10^{-4}	5.0×10^{-3}	8.2×10^{-5}	7.0×10^{-3}	0.013	7.8×10^{-3}	0.065	0.039
Regional	1.6×10^{-4}	3.7×10^{-3}	1.1×10^{-4}	9.4×10^{-3}				

Notes: [1]The values for predators use a BMF_1 of 4.6.
[2]The values for top predators use a BMF_1 and BMF_2 of 4.6.

5.5.2 Assessment against PBT criteria

D4 is not considered readily biodegradable, but it does degrade in water by hydrolysis. According to the TGD, the relevant environmental conditions for marine waters are a pH of around 8 and a temperature of 9°C. From the data available the best estimate of the hydrolysis half-life at 9°C is 2.9 days at pH 8. Thus at pHs around 8 the hydrolysis half-life for D4 is clearly below the threshold set for the persistent (P) and very persistent (vP) criteria (both of which use a half-life of 60 days in marine water). Similarly, the hydrolysis half-life at pH 7 and 12°C is estimated as 16.7 days. The main product from the hydrolysis reaction is known to be dimethylsilanediol, which is itself unlikely to posses PBT properties. Therefore, on this basis D4 does not meet the P or vP criteria.

As well as hydrolysis, D4 is likely to be rapidly lost from water by volatilisation. However, in water D4 is also expected to adsorb onto sediment to some extent and the adsorbed D4 may then not be available for rapid hydrolysis. The results of preliminary experiments to examine the disappearance of D4 from a static sediment–water–air system at room temperature recently became available (see Section 3.2.2). Under laboratory conditions the half-life in the sediment phase for D4 approaches the 120 day cut-off for a P substance for sediment, which indicates that D4 may meet the P criteria in terms of persistence in sediment. However, these studies are on-going, and only brief details are currently available. The results of these studies are potentially important to the overall conclusions of the PBT assessment for D4, and so this assessment should be revisited once the study is complete and full details are available.

Although the limited information currently available suggests that the half-life of D4 in sediment could approach 120 days, mitigating factors should be taken into account in this respect. In particularD4 is highly volatile and so transfers readily from the aquatic compartment to the atmosphere, where it degrades. This, and the reasonably rapid rate of hydrolysis of D4, means that significant and rapid removal of D4 from the water phase is likely, which results relatively low concentrations in this phase. This type of behaviour in aquatic systems is predicted for D5 (Environment Agency, 2008a) using a series of models. Here it is found that, although the predicted persistence in sediment is itself not affected by volatility, the predicted concentration is significantly reduced by volatility as a consequence of the reduced water column concentrations. However, D4 is found in some sediments, and so its persistence in sediment is a relevant consideration.

For the bioaccumulation criterion, the substance has a fish BCF of 12,400 and so clearly meets the very bioaccumulative (vB) criterion.

D4 has a long-term fish NOEC ≥4.4 µg/l (limit value at which no effects ware seen) and a NOEC of 7.9 µg/l with *D. magna* (adverse effects seen at higher concentrations). In addition, D4 is classified as a category 3 reprotoxicant. Therefore the substance meets the toxic (T) criterion.

Overall, it is concluded that D4 may meet the P criterion based on its possible persistence in sediment and does meet the vB and T criteria. Therefore, it can be considered a potential PBT substance. However, the available information on persistence in sediments is currently limited and further work is on-going, so this conclusion should be revisited once this work is completed.

In relation to the PBT assessment the long-range transport potential for D4 is also relevant, as the atmosphere is a potentially important environmental compartment for it. The available information indicates that, although D4 has the potential to be transported long distances in the atmosphere, its properties mean that it has a low

potential for redeposition to surface media in remote regions (see Section 5.3). The recent modelling studies by Xu (2007b, 2007c) support this conclusion.

The first model investigated was the OECDPov and LRTP screening tool (Xu, 2007b). The properties (all at 25°C) for D4 assumed in the simulation are log K_{aw} 2.69, log K_{ow} 6.49, half-life in air 248 hours, half-life in water 93.5 hours, and half-life in soil 127 hours [estimated for a temperate soil at a dryness equivalent to 90 per cent relative humidity, based on Xu (2007a); see Section 3.2.3]. The model default values are used for compartment dimensions and properties. Various emission patterns considered assumed, firstly, 100 per cent emission to either air, water, or soil, then equal emissions to air, water, and soil, and finally (considered to be more realistic) 99.6 per cent of the total emission to air, 0.004 per cent to water, and 0.4 per cent to soil.

The outputs from the models include the overall persistence, characteristic travel distance, and transfer efficiency. These are then used to determine the priority of the chemical in terms of long-range transport potential.

The maximum values for the overall persistence, characteristic travel distance, and transfer efficiency in the various simulations are 14.9 days (when 100 per cent release to air is assumed[25]), 5121 km (when 100 per cent release to air is assumed), and 1.5×10^{-2} per cent (when 100 per cent release to air is assumed), respectively. From these modelling studies, D4 is identified as a low priority chemical based on the criteria used in the OECD screening tool.

The second model considered was the GLOBOPOP model (Xu, 2007c). The same physicochemical properties and degradation rates as above are assumed, but additionally a degradation half-life of 4020 hours (17 days) in sediments was also used.[26] All simulations were carried out using the model default values for the compartment dimensions and properties. The total D4 emission rate assumed was 3×10^7 kg/year, with and assumed 80 per cent released from the northern temperate climate zone, 15 per cent from the northern subtropical zone, and 5 per cent from the northern tropical zone. Within each climate zone, the release is estimated as 99.6 per cent to air, 0.003 per cent to freshwater, and 0.4 per cent to agricultural soil (this is considered to be a realistic emission scenario based on the known uses of D4). No seasonal variation of emission is assumed.

The time to reach steady state within the model is estimated as 2–3 years for air and soil, but longer for water and sediment (4–10 years for water and 4–25 years for sediment). The relative Arctic contamination potential is very low (around 0.003 per cent after ten years continuous release; this value is less than 0.001 that of hexachlorobenzene and PCB-101). The absolute Arctic contamination potential after ten years continuous release is 9×10^{-5} per cent (this value is less than 0.00005 that of hexachlorobenzene and 0.0001 that of PCB-101. It is also predicted that the amount of D4 that accumulates in polar surface media is very low (0.001 per cent of the total release in any period), and the amount of D4 that remains in polar surface media at any one time is also low (<0.003 per cent of the total D4 that remains in the model). It is also estimated that around 92 per cent of the D4 degrades after four years continuous release and close to 97 per cent of D4 does so after ten years of continuous release. After ten years continuous release it is predicted that the majority (99.8 per cent) of the D4 that remains within the system is in the air compartment and, of the remaining 0.2 per cent in surface media, the majority of this (70 per cent) is in the soil and sediment compartments of the three source zones (northern temperate, northern subtropical, and northern tropical zones).

[25]It is not entirely clear from the paper which simulation led to this value.
[26]It is not clear how this value is derived. The half-life used appears to be short compared with the available data for degradation of D4 sediment.

Overall, these new studies suggest that, although D4 can be transported to remote regions to some extent via the atmosphere, significant deposition in remote regions is unlikely. However, these simulations assume a relatively rapid degradation rate in soil (and in one case sediment) for D4. The degradation rate used may not be appropriate for soils with high water contents.

5.5.3 Uncertainties and possible refinements

Similar to the freshwater assessment there are problems the PECs for marine water, sediment, and secondary poisoning of marine predators and marine top predators. Further exposure information is needed to refine the PEC estimates. Further information on the toxicity to sediment-dwelling organisms would help refine the PNEC for marine sediment. It may be possible to further refine the PNEC for marine water by carrying out further toxicity testing.

There is some uncertainty over the BMF used for predators and top predators. The default value for the BMF_1 and BMF_2 is 10. These default values may not be appropriate for D4 and so a kinetic, growth-corrected, and lipid-normalised BMF of 4.6 is used in the assessment for both BMF_1 and BMF_2.

In relation to the PBT assessment, D4 is lost rapidly from surface water by volatilisation, but may also adsorb to sediment where it may be more persistent than in surface water itself. Experimental and modelling work on the persistence in sediment is currently being carried out for both D4 and D5 to help determine the effect of volatilisation on the half-life in sediment. The results of this work may be useful in relation to the overall conclusions of the PBT assessment for D4.

Some uncertainty exists in the log K_{ow} and K_{oc} values for D4. In Appendix A we consider the effect of using a higher log K_{ow} value on the outcome of the marine compartment. This approach again indicates possible risks to marine water (one scenario) and marine sediment (four scenarios). A measured K_{oc} value would be useful to confirm or refine the PECs for these scenarios.

5.5.4 Conclusions for the marine compartment

Based on the available information D4 potentially meets the criteria for a PBT substance when the persistence in sediment is considered. However, the available information on persistence in sediments is limited, and as further work is on-going this conclusion should be revisited once this work is completed. It is thought that D4 is unlikely to meet the POPs screening criteria in relation to long-range transport potential.

Worst-case PEC/PNEC ratios are >1 for marine water and sediment for two scenarios (production and on-site use as an intermediate and the generic scenario for formulation of personal care products) and are >1 for predators and top predators for one scenario (production and on-site use as an intermediate). Further information is needed to refine the PEC calculations for these endpoints. Information provided for D4 for UK sites and for other EU sites for D5 suggests that the generic scenario for formulation of personal care products is overly conservative for such sites, both in the UK and in the EU as a whole, so the actual risk to the marine environment from this scenario is low. In addition, further information may be needed to refine the PNECs for marine water and sediment.

5.6 Man exposed via the environment

For humans exposed via the environment, the local effects on the respiratory tract are not critical as inhalation exposures are low when dissipated through the environment. Therefore, the most important health effect is liver enlargement after repeated exposure. The oral route contributes by far the most significant fraction to the total dose to which humans are exposed via the environment. Therefore, the oral NOAEL of 25 mg/kg/day identified for this effect from a 14 day gavage study in rats based on a 17 per cent increase in liver weight at the next highest dose is used in the risk assessment.

This NOAEL, which is the toxicological starting point for the risk characterisation of D4, is obtained from studies in rats, so to conduct the risk characterisation, extrapolation from rats to humans is needed. The available evidence indicates that it is unlikely that humans are more sensitive than rats to phenobarbital-like enzyme induction and subsequent liver enlargement. In studies of epileptic patients treated with therapeutic doses of phenobarbital, which are equivalent to those that cause large increases in liver weight in rats, no significant increase in liver pathology, or significant abdominal organ compression caused by increased liver weight or toxicity has occurred (Olsen *et al*., 1989). On this basis, an AF for interspecies differences of one seems appropriate. However, given the limitations of these human data (no accurate quantitative information on the magnitude of the effects and lack of detailed investigations) a more conservative interspecies AF of two is selected.

In relation to intraspecies differences, phenobarbital-like liver enzyme induction and subsequent liver enlargement (from 10 per cent and above) are likely to have adverse consequences only in the most susceptible individuals of the population. Therefore, the default intraspecies AF of ten can be lowered to five.

Finally, the oral NOAEL for the risk characterisation is identified from a 14 day study. However, human exposure to D4 via the environment is likely to be chronic. Therefore, an additional AF of ten is selected to extrapolate for duration of exposure.

An overall minimal margin of safety (minMOS) of 100 ($2 \times 5 \times 10$) is therefore established for this effect. The maximum continuous human exposure from local environmental sources predicted by EUSES is 0.082 mg/kg body weight/day in the vicinity of production sites and use-as-an-intermediate sites within the UK (see Section 0). The MOS between the NOAEL for liver enlargement (25 mg/kg/day) and this exposure level is 304. This MOS value is greater than the minMOS of 100 and so there is no concern for local exposures (doubt would exist if the minMOS was higher than the MOS).

The value for human exposure from regional environmental sources predicted by EUSES is 3.6×10^{-4} mg/kg body weight/day. The MOS between the NOAEL for liver enlargement (25 mg/kg/day) and this exposure level is 6.9×10^{4}, which significantly greater than the minMOS of 100. Therefore there is no concern for regional exposures.

5.7 Further testing currently underway

A number of further tests and studies with D4 of direct relevance to the conclusions of this assessment are (or are in the process of being) commissioned by CES (2007) on a voluntary basis.

The studies include:

- atmospheric degradation – evaluation of additional degradation pathways to better understand the degradation in the atmosphere and long-range transport potential;
- degradation in sediment under aerobic and anaerobic conditions (modified OECD 308 method);
- further modelling of the environmental distribution and overall fate;
- further sediment toxicity study with Lumbriculus species;
- in vivo metabolism and kinetics study with fish after oral exposure;
- bioaccumulation – physiologically based pharmacokinetic (PBPK) modelling of fish;
- bioaccumulation – extension of PBPK model from fish and mammals to other environmental species;
- environmental monitoring of air, sewage effluent, river water, sediment, and biota including:
    - Lake Pepin, MN, to look at historical deposition patterns to evaluate degradation in the environment,
    - CES mussel screening program (preliminary results from this study are included in this risk assessment),
    - River Nene to look at the distribution and persistence downstream from a known point source (monitoring and river die-away study),
    - Long-term robust monitoring program to investigate the persistence and bioaccumulation potential in the field, but it has yet to be developed fully and agreed, although it is likely to include investigations of time trends (using freshwater and marine sediment cores from local, regional, and remote locations and from archived biota samples), spatial distributions (sampling sediment and biota along transects of freshwaters from local, regional, and remote locations), and air samples (from local, regional, and remote locations),
    - site-specific monitoring to refine the current PECs used in the risk assessment;
- development of analytical methodology for water, sediment, soil, biota, sludge, and air to support these studies.

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List of abbreviations

AIChE	American Institute of Chemical Engineers
BCF	Bioconcentration factor
BMF	Biomagnification factor
CES	Centre Européen des Silicones
cst	Centistokes
CTPA	Cosmetic, Toiletry and Perfumery Association
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
D7	Tetradecamethylcycloheptasiloxane
DIPPR	Design Institute for Physical Property Data
EC_{50}	50 per cent Effect concentration
EPICS	Equilibrium Partitioning in Closed Systems
EUSES	European Union System for the Evaluation of Substances
HAV	Heat-activated vulcanising
IC	Industry Category
ITC	Interagency Testing Committee
IUCLID	International Uniform Chemical Information Database
K_{aw}	Air–water partition coefficient
K_{oa}	Octanol–air partition coefficient
K_{ow}	Octanol–water partition coefficient
K_{sed}	Solids–water partition coefficient in sediment
$K_{sed-water}$	Sediment–water partition coefficient
K_{soil}	Solids–water partition coefficient in soil
$K_{soil-water}$	Soil–water partition coefficient
K_{susp}	Solids–water partition coefficient in suspended matter
$K_{susp-water}$	Suspended matter–water partition coefficient (
LC_{50}	Lethal concentration 50 – the concentration that kills 50 per cent of the population
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
MC	Main Category
MQ resins	MQ resins are composed of clusters of quadrafunctional silicate groups (commonly termed Q groups) end-capped with monofunctional trimethylsiloxy groups (commonly termed M groups)
LC_{50}	Lethal concentration 50 – the concentration that kills 50 per cent of the population
LOAEL	Lowest observe adverse effect level
LOQ	Limit of quantification
NIK	Niedrigste Interessierende Konzentration
NOEC	No observed effect concentration
OECD	Organisation for Economic Co-operation and Development
PBPK	Physiologically based pharmacokinetic
PBT	Persistent, bioaccumulative and toxic
PDMS	Polydimethylsiloxane
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
POP	Persistent organic pollutant
POCP	Photochemical ozone creation potential
ppm	Parts per million

ppm_v	Parts per million by volume
ppb	Parts per billion
ppb_v	Parts per billion by volume
RTV	Room temperature vulcanising
TD resins	TD resins contain difunctional dimethylsiloxy groups (commonly termed D groups) and trifunctional methylsiloxy groups (commonly termed T groups)
TGD	Technical Guidance Document
TSCA	Toxic Substances Control Act
UC	Use Category
USEPA	United States Environmental Protection Agency
VMS	Volatile methylsiloxanes
vPvB	Very persistent, very bioaccumulative

Appendix A: Sensitivity of the assessment to the values of log K_{ow} and Henry's law constant

As discussed in Section 1 of the main report, new values for the log K_{ow} and Henry's law constant for D4 became available recently. Few experimental details are currently available as to how these values were determined and so, at this stage, it is not possible to conclude which value is most reliable for these parameters. The main risk assessment is carried out using a log K_{ow} value of 6.49 and a Henry's law constant of 1.21×10^6 Pa m^3/mol at 25°C. In this Appendix we consider the consequences of assuming lower values for the log K_{ow} (5.1) and Henry's law constant (60,060 Pa m^3/mol at 28°C) on the outcome of the risk assessment.

The EUSES model was run for the generic scenarios using the input parameters:

- log Kow = 5.1
- Henry's law constant = 60,060 Pa m3/mol
- Koc = 1.7 × 104 l/kg
- fish BCF =12,400 l/kg
- BMF = 4.6.

As the K_{oc}, BCF, and BMF are measured for D4, and the values are considered reliable, these measured values are used in the analysis here rather than estimates of the values from log K_{ow}.

Both log K_{ow} and Henry's law constant affect the predicted partitioning of D4 in the environment. The most important partition coefficients used in the assessment derived from these values are:

- Koc, 1.7 × 104 l/kg
- Ksoil, 340 l/kg
- Ksed, 850 l/kg
- Ksusp, 1.7 × 103 l/kg
- Ksoil–water, 520 m3/m3
- Ksusp–water, 430 m3/m3
- Ksed–water, 430 m3/m3.

With the exception of the $K_{soil–water}$ these derived partition coefficients are the same as those used in the main assessment (the $K_{soil–water}$ has a small dependence on the Henry's law constant).

The expected behaviour during wastewater treatment is estimated using the Simpletreat model within EUSES 2.0.3, and is identical to the behaviour estimated in the main report.

- 48.2 per cent to air
- 48.2 per cent to sludge
- 0 per cent degraded
- 3.59 per cent to water.

The log K_{ow} potentially affects any PNECs determined by the equilibrium partitioning method. For D4, only the PNEC for soil is estimated using this method, and it depends on the soil–water partition coefficient ($K_{soil–water}$). The effect on the PNEC for soil of using a lower Henry's law constant and log K_{ow} is only very minor as the $K_{soil–water}$ is reduced from 610 m^3/m^3 to 520 m^3/m^3, since it is estimated based on the measured K_{oc} value. The PNEC for soil estimated using the lower $K_{soil–water}$ value is 0.13 mg/kg wet weight.

Based on the above, use of the alternative log K_{ow} and Henry's law constant is expected to have only a very minor impact on the outcome of the risk assessment. The PEC and risk characterisation ratios obtained using a log K_{ow} of 5.1 and a Henry's law constant of 60,060 Pa m^3/mol are summarised in Tables A1 to A6.

Table A1 Risk characterisation ratios for surface water

Scenario	PEC (µg/l)	Risk characterisation ratio[1]
Production and on-site use as an intermediate – UK site	3.9	8.9
Off-site use as an intermediate – polymers – wet process – UK sites	7.5×10^{-3}	0.017
Off-site use as an intermediate – polymers – wet process – EU sites	2.4×10^{-3}	5.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	2.4×10^{-3}	5.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – EU sites	2.4×10^{-3}	5.5×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	2.4×10^{-3}	5.5×10^{-3}
Personal care products – formulation – generic site (non-UK)	0.018	0.041
Personal care products – use by general public	9.0×10^{-3}	0.020
Household products – formulation	7.6×10^{-3}	0.017
Household products – use	3.0×10^{-3}	6.8×10^{-3}
Regional	2.4×10^{-3}	5.5×10^{-3}

Note: [1]Indicative concentration is 0.44 µg/l.

Table A2 Risk characterisation ratios for sediment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	1.5	13
Off-site use as an intermediate – polymers – wet process – UK sites	2.8×10^{-3}	0.024
Off-site use as an intermediate – polymers – wet process – EU sites	8.8×10^{-4}	7.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	8.8×10^{-4}	7.5×10^{-3}
Off-site use as an intermediate – polymers – dry process – EU sites	8.8×10^{-4}	7.5×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	8.8×10^{-4}	7.5×10^{-3}
Personal care products – formulation – generic site (non-UK)	6.7×10^{-3}	0.057
Personal care products – use by general public	3.3×10^{-3}	0.028
Household products – formulation	2.8×10^{-3}	0.024
Household products – use	1.1×10^{-3}	9.4×10^{-3}
Regional	1.7×10^{-3}	0.015

Note: [1]PNEC is 0.12 mg/kg wet weight.

Table A3 Risk characterisation ratios for the soil compartment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	1.2×10^{-3}	0.093
Off-site use as an intermediate – polymers – wet process – UK sites	4.9×10^{-3}	0.37
Off-site use as an intermediate – polymers – wet process – EU sites	2.2×10^{-5}	1.7×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	2.8×10^{-6}	2.1×10^{-4}
Off-site use as an intermediate – polymers – dry process – EU sites	4.6×10^{-4}	0.034
Off-site use as an intermediate – silica – UK and EU sites	1.2×10^{-5}	9.2×10^{-4}
Personal care products – formulation – generic site (non-UK)	2.2×10^{-3}	0.17
Personal care products – use by general public	9.4×10^{-4}	0.070
Household products – formulation	7.4×10^{-4}	0.056
Household products – use	8.4×10^{-5}	6.3×10^{-3}
Regional – agricultural soil	8.4×10^{-4}	0.063
Regional – natural soil	9.7×10^{-8}	7.5×10^{-6}
Regional – industrial soil	9.7×10^{-8}	7.5×10^{-6}

Note: [1]PNEC is 0.13 mg/kg wet weight. The ratios are increased by a factor of 10 in line with the recommendations in the TGD.

Table A4 Risk characterisation ratios for secondary poisoning

Scenario	Fish		Earthworms	
	PEC (mg/kg)	Risk characterisation ratio[1]	PEC (mg/kg)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	112	67	4.7×10^{-3}	2.8×10^{-3}
Off-site use as an intermediate – polymers – wet process – UK sites	0.21	0.13	3.8×10^{-3}	2.3×10^{-3}
Off-site use as an intermediate – polymers – wet process – EU sites	0.17	0.10	1.9×10^{-3}	1.1×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	0.17	0.10	1.9×10^{-3}	1.1×10^{-3}
Off-site use as an intermediate – polymers – dry process – EU sites	0.17	0.10	2.9×10^{-3}	1.7×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	0.17	0.10	1.9×10^{-3}	1.1×10^{-3}
Personal care products – formulation – generic site (non-UK)	0.62	0.37	2.7×10^{-3}	1.6×10^{-3}
Personal care products – use by general public	0.40	0.24	2.2×10^{-3}	1.3×10^{-3}
Household products – formulation	0.32	0.19	2.1×10^{-3}	1.3×10^{-3}
Household products – use	0.19	0.11	1.9×10^{-3}	1.1×10^{-3}

Note: [1]PNEC is 1.7 mg/kg food.

Table A5 Risk characterisation ratios for secondary poisoning for the marine environment

Scenario	Predators		Top predators	
	PEC (mg/kg)	Risk characterisation ratio[1]	PEC (mg/kg)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	2.8	1.7	3.2	1.9
Off-site use as an intermediate – polymers – wet process – UK sites	0.045	0.027	0.10	0.060
Off-site use as an intermediate – polymers – wet process – EU sites	0.011	6.6×10^{-3}	0.063	0.038
Off-site use as an intermediate – polymers – dry process – UK sites	0.011	6.6×10^{-3}	0.063	0.038
Off-site use as an intermediate – polymers – dry process – EU sites	0.011	6.6×10^{-3}	0.063	0.038
Off-site use as an intermediate – silica – UK and EU sites	0.011	6.6×10^{-3}	0.063	0.038
Personal care products – formulation – generic site (non-UK)	1.3	0.78	1.5	0.90
Personal care products – use by general public	0.034	0.020	0.089	0.053
Household products – formulation	0.43	0.26	0.53	0.32
Household products – use	0.013	7.8×10^{-3}	0.065	0.039

Note: [1]PNEC is 1.7 mg/kg food.

Table A6 Risk characterisation ratios for marine water and sediment

Scenario	Marine water		Marine sediment	
	PEC (µg/l)	Risk characterisation ratio[1]	PEC (mg/kg)	Risk characterisation ratio[2]
Production and on-site use as an intermediate	0.099	2.3	0.037	3.2
Off-site use as an intermediate – polymers – wet process – UK sites	3.7×10^{-3}	0.083	1.4×10^{-3}	0.12
Off-site use as an intermediate – polymers – wet process – EU sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}
Off-site use as an intermediate – polymers – dry process – UK sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}
Off-site use as an intermediate – polymers – dry process – EU sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}
Off-site use as an intermediate – silica – UK and EU sites	1.6×10^{-4}	3.7×10^{-3}	6.0×10^{-5}	5.1×10^{-3}
Personal care products – formulation - generic site (non-UK)	0.044	1.0	0.016	1.4
Personal care products – use by general public	8.3×10^{-4}	0.019	3.1×10^{-4}	0.026
Household products – formulation	0.015	0.34	5.5×10^{-3}	0.47
Household products – use	2.2×10^{-4}	5.0×10^{-3}	8.2×10^{-5}	7.0×10^{-3}
Regional	1.6×10^{-4}	3.7×10^{-3}	1.1×10^{-4}	9.4×10^{-3}

Note: [1]PNEC for marine water is 0.044 µg/l.
[2]PNEC for marine sediment is 0.012 mg/kg wet weight.

This analysis leads to essentially the same conclusions as those in the main risk assessment report for all endpoints.

Appendix B: Summary of ecotoxicity data

This Appendix contains summary tables of the available ecotoxicity data. Where possible, a validity marking is given for each study (this appears in the summary tables within each Section). The validity markings used are:

Valid without restriction. The test is carried out to internationally recognised protocols (or equivalent protocols) and all or most of the important experimental details are available.

Use with care. The test is carried out to internationally recognised protocols (or equivalent protocols) but some important experimental details are missing, or the method used, or endpoint studied, in the test means that interpretation of the results is not straight forward.

Not valid. There is a clear deficiency in the test that means that the results cannot be considered as valid.

Not assignable. Insufficient detail is available on the method used to allow a decision to be made on the validity of the study.

These validity codes are based on the Klimisch codes used by the OECD.

Table B1 Summary of short-term toxicity to freshwater fish1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O.					
Brachydanio rerio										Static (open)		Mortality		96 hour LC_{50} >500 mg/l	Firmin *et al.*, 1984	**3**
Lepomis macrochirus										Static (open)		Mortality		96 hour LC_{50} >1000 mg/l	Firmin *et al.*, 1984	**3**
Leuciscus idus	DEV L15									Static (open)		Mortality		96 hour LC_0 = 200 mg/l	IUCLID (2005)	**3**
										Flow		Mortality		96 hour LC_{50} >1041 mg/l	IUCLID (2005)	**3**
Oncorhynchus mykiss	40 CFR 797.1400 (modified)	20 in two replicates – loading 0.17 g/l	0.42 g	2.9, 4.4, 6.9, 12, and 22 µg/l plus control	M	Well water	12	28–36 mg/l	6.8–7.2	Flow		Mortality	5% mortality	14 day LC_{50} = 10 µg/l 14 day NOEC = 4.4 µg/l	Sousa *et al.*, 1995	**2**
	OECD 204			0, 5.7, 9.4, 16.9, 34.2, and 51.7 µg/l plus control	M							Behaviour		14 day NOEC = 16.9 µg/l	IUCLID, 2005	**4**
			Small fish									Mortality		18 day LC_{80} = 23 µg/l	IUCLID, 2005	**4**
			Large fish (5 g)									Mortality		18 day LC_0 ≥31 µg/l	IUCLID, 2005	**4**
										Static (open)		Mortality		96 hour LC_{50} = >1000 mg/l	Firmin *et al.*, 1984	**3**

Notes: [1]N or M = nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/l, Sal., salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val., validity marking.

Table B2 Summary of short-term toxicity to marine fish1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Sal.	pH	Static/ flow	D.O.					
Cyrpinodon variegatus	40 CFR 797.1400 (modified)	20 in two replicates – loading 0.14 g/l	0.33 g	1.3, 1.6, 2.3, 4.2, and 6.3 µg/l plus control	M	Natural sea water	25	31–32‰	7.8-8.0	Flow		Mortality	5% mortality	14 day LC50 >6.3 µg/l 14 day NOEC ≥6.3 µg/l	Sousa *et al.*, 1995	**2**
Fundulus heterolitus										Static (open)				96 hour LC_{50} >1000 mg/l	Firmin *et al.*, 1984	**3**

Notes: [1]N or M, nominal or measured concentration, Temp, temperature, Hard., water hardness as mg $CaCO_3$/l, Sal., salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val., validity marking.

Table B3 Summary of long-term toxicity to freshwater fish1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O.					
Oncorhynchus mykiss	40 CFR 797.1600 (modified)	100 eggs in four replicates, 60 larvae in 4–6 replicates	Egg larva	0.25, 0.53, 1.1, 1.9, and 4.4 µg/l plus control	M	Well water	12	28–36 mg/l	6.8–7.2	Flow	>84 %	Embryo viability	77% viability	19 day NOEC ≥4.4 µg/l	Sousa *et al*., 1995	**2**
												Survival at hatch	80% survival	33 day NOEC ≥4.4 µg/l		
												Survival days 0–45 post-hatch	97% survival	78 day NOEC ≥4.4 µg/l		
												Survival days 45–60 post-hatch	100% survival	93 day NOEC ≥4.4 µg/l		
												Growth at 90 days post hatch	Mean length 53 mm Mean wet weight 1.6 g	93 day NOEC ≥4.4 µg/l		

Notes: [1]N or M, nominal or measured concentration; Temp., temperature.; Hard., water hardness as mg $CaCO_3$/l; Sal., salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val. = validity marking.

Table B4 Summary of short-term toxicity to freshwater invertebrates1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O.					
Daphnia magna	40 CFR 797.1300 (modified)	20 in two replicates	<24 hours	1.7, 2.9, 3.7, 7.8, and 15 µg/l plus control	M	Well water	20	160–180 mg/l		Flow	>60 %	Immobile	0% immobilis-ation	48 hour EC_{50} >15 µg/l 48 hour NOEC ≥15 µg/l	Sousa *et al.*, 1995	**2**
	UBA			Hard castor oil used as solubility promoter						Static				24 hour EC_0 = 3.1 mg/l 24 hour EC_{50} = 25.2 mg/l 24 hour EC_{100} = 314 mg/l	IUCLID, 2005	**3**

Notes: [1]N or M, nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/l; Sal., salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val., validity marking.

Table B5 Summary of short-term toxicity to marine invertebrates1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Sal.	pH	Static/ flow	D.O.					
Artemia salina														24 hour EC_{50} >500 mg/l	Firmin *et al*., 1984	**3**
Crangon crangon														96 hour EC_{50} >1000 mg/l	Firmin *et al*., 1984	**3**
Mysidopsis bahia	40 CFR 797.1930 (modified)	20 in two replicates	<24 hours	1.6, 2.2, 3.7, and 9.1 µg/l plus control	M	Diluted sea water	25	20‰	7.9–8.1	Flow		Mortality	0% mortality	96 hour LC_{50} >9.1 µg/l 96 hour NOEC ≥9.1 µg/l	Sousa *et al*., 1995	**2**

Notes: [1]N or M, nominal or measured concentration; Temp., temperature; Hard, water hardness as mg $CaCO_3$/l; Sal., salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val., validity marking.

Table B6 Summary of long-term toxicity to freshwater invertebrates1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O.					
Chironomus tentans		50	2nd instar	0.49, 1.2, 2.9, 6.5, and 15 µg/l plus control	M	Well water	22	20–40 mg/l	6.9–7.5	Flow		Survival	88% survival	14 day NOEC ≥15 µg/l	Kent *et al*., 1994	**2**
												Growth	Mean organism wet weight = 23 mg	14 day NOEC ≥15 µg/l		
Daphnia magna	40 CFR 797.1330 (modified)	30 in two replicates	<24 hours	1.7, 1.8, 4.2, 7.9, and 15 µg/l plus control	M	Well water	22	28–36 mg/l	7	Flow	>60 %	Survival	93% survival	21 day NOEC = 7.9 µg/l	Sousa *et al*., 1995	**2**
												Reproduction	111 offspring per female daphnid	21 day NOEC ≥7.9 µg/l		

Notes: [1]N or M, nominal or measured concentration; Temp, temperature; Hard, water hardness as mg $CaCO_3$/l; Sal, salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val., validity marking.

Table B7 Summary of short-term toxicity to freshwater algae and plants1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O.					
Anabaena flos-aquae														EC50 > 2000 mg/l	Firmin et al., 1984	**3**
Pseudokirchneriella subcapitata	TSCA Test Standard No 797-1050			22 µg/l plus control	M							Growth rate		96 hour EC_{50} >0.022 mg/l	IUCLID, 2005	**3**

Notes: [1]N or M, nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/l; Sal., salinity; D.O., dissolved oxygen (either as percentage saturation or mg O_2/l); Val., validity marking.

[2]Formerly *Selenastrum capricornutum*.

Table B 8 Summary of sediment toxicity data1

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions			Endpoint	Control response	Effect concentration	Reference	Val.
						O.C. (%)	Hard.	pH					
Chironomus riparius	OECD 218	20 per replicate, four replicates per treatment group	1–3 day old	6.5, 7.9, 19, 44, 131, and 355 mg/kg dry weight plus control	M	4.1	140–154	8.2–8.6	Survival	91.2% survival	28 day NOEC = 44 mg/kg dry weight 28 day LC_{50} = 114 mg/kg dry weight	Krueger *et al.*, 2008	**1**
									Development time	Mean development time 18.4 days	28 day NOEC = 131 mg/kg dry weight		
									Emergence ratio	Mean emergence ratio 0.93	28 day NOEC = 44 mg/kg dry weight		
									Development rate	Mean development rate 0.0572	28 day NOEC = 131 mg/kg dry weight		

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions			Endpoint	Control response	Effect concentration	Reference	Val.
						O.C. (%)	Hard.	pH					
Chironomus tentans		50	2nd instar	6.8, 17, 32, 65, and 130 mg/kg dry weight plus control and solvent control	M	0.27	20–40	6.9–7.5	Survival	81% survival (pooled control)	14 day NOEC ≥130 mg/kg dry weight	Kent *et al*., 1994; Springborn Laboratories, 1991a	**2**
									Growth	Mean larval wet weight 23 mg (pooled control)	14 day NOEC = 65 mg/kg wet weight		
				18, 38, 76, 120, and 250 mg/kg dry weight plus control and solvent control	M	2.3	20–40	6.9–7.5	Survival	69% survival (pooled control)	14 day NOEC = 120 mg/kg dry weight	Kent *et al*., 1994; Springborn Laboratories, 1991a	**3**
									Growth	Mean larval wet weight 23 mg (pooled control)	14 day NOEC ≥250 mg/kg dry weight		
				2.6, 7.4, 19, 54, and 170 mg/kg dry weight plus control and solvent control	M	4.1	20–40	6.9–7.5	Survival	89% survival (pooled control)	14 day NOEC = 54 mg/kg dry weight	Kent *et al*., 1994; Springborn Laboratories, 1991b	**2**
									Growth	Mean larval wet weight 16 mg (pooled control)	14 day NOEC ≥170 mg/kg dry weight		
				16, 32, 59, 110, and 200 mg/kg dry weight plus control and solvent control	M	3.9	20–40	6.9–7.5	Survival	73% (pooled control)	14 day NOEC <16 mg/kg dry weight	Walker, 1993; Springborn Laboratories, 1991a	**3**

Notes: [1]N or M, nominal or measured concentration; Temp, temperature; Hard, water hardness as mg $CaCO_3$/l; O.C., organic carbon content.

Val. = Validity marking.

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